ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECT OF SCREW ROTATION SPEED, COMPATIBILIZER AND R-PET CONCENTRATION ON PROPERTIES OF R-PET/HDPE BLENDS

M.Sc. THESIS

Tuğba GÜVEN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2015

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECT OF SCREW ROTATION SPEED, COMPATIBILIZER AND R-PET CONCENTRATION ON PROPERTIES OF R-PET/HDPE BLENDS

M.Sc. THESIS

Tuğba GÜVEN
(515111044)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. F. Seniha GÜNER

JANUARY 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

VİDA DÖNÜŞ HIZININ, UYUMLAŞTIRICI VE R-PET MİKTARININ R-PET/HDPE HARMAN ÖZELLİKLERİNE ETKİSİ

YÜKSEK LİSANS TEZİ

Tuğba GÜVEN
(515111044)

Polimer Bilimi ve Teknoloji Anabilim Dalı

Polimer Bilimi ve Teknoloji Programı

Tez Danışmanı: Prof. Dr. F. Seniha GÜNER

OCAK 2015

Tuğba Güven, a **M.Sc.** student of ITU Institute of Science and Technology of student 515111044, successfully defended the thesis entitled "EFFECT OF SCREW ROTATION SPEED, COMPATIBILIZER AND R-PET CONCENTRATION ON PROPERTIES OF R-PET/HDPE BLENDS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. F. Seniha GÜNER** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Oya ATICI** İstanbul Technical University	.....
	Prof. Dr. Sermet KABASAKAL Eskişehir Osman Gazi University	.....

Date of Submission : 15 December 2014
Date of Defense : 21 January 2015

To my family,

FOREWORD

This thesis was supported by the scope of the project SAN-TEZ.
First and foremost, I would like to express my special gratitude to my supervisor Prof. Dr. F. Seniha GÜNER for her scientific support, thoughtfully comment on several drafts and advice towards the completion of this study.
I am very grateful to İsminur ERKOÇ because of all her support, practical, technical and theoretical help in any aspect of the work and she always cheered me up whenever I got problems in the work.
Especially thank to my teammates Fatih YILDIRIM for helping me during the extrusion process.
Many thanks to Betül KAHRAMAN for her kind help in the mechanical analysis.
I thank to Büşra KARAMAN for helping me for the FTIR analysis
I gratefully acknowledge the financial support of Mir ARGE, also the financial support of ministry of industry under Project 0460.STZ.2013-2. In addition
I appreciate the valuable help and advice of the Mir R&D materials and chemistry director of Mustafa DOĞU. I would like to thank the Mir ARGE for providing me the opportunity of working in their laboratories.
Finally I wish to thank to especially my home friends Damla ÇALIM, Buse DOMBAYCI and Aylin GENÇÜNAL for their friendship and support.
My special thanks to my parents and brother for moral support and belief in me always.

January 2015

Tuğba GÜVEN
Chemical Engineering

TABLE OF CONTENTS

Page

ABBREVIATIONS

PE : Polyethylene
HDPE : High Density Polyethylene
R-PET : Recycled Polyethylene Terephthalate
SEBS : Styrene-Ethylene / Butylene-Styrene
E-GMA : Ethylene Glycidyl Methacrylate Copolymer
E-EA-GMA : Ethylene Ethylacrylate Glycidyl Methacrylate Terpolymer
SEBS-g-MA : Hydrogenated Styrene-Butadiene-Styrene Copolymer Grafted with Maleic Anhydride
E-MeA-g-MA: Modified Ethylene-Methylacrylate Copolymer
SEM : Scanning Electron Microscope
MFI : Melt Flow Index
MDI : 4,40- 4,40-methylenedi(phenyl isocyanate)
FTIR : Fourier Transforms Infrared Spectroscopy
ΔGmix : Gibbs energy of mixing
ΔHm : Enthalpy of mixing
ΔSm : Entropy of mixing
Tg : Glass transition
DSC : Differential Scanning Calorimetry

LIST OF TABLES

Page

LIST OF FIGURES

Page

EFFECT OF SCREW ROTATİON SPEED, COMPATIBILIZER AND R-PET CONTENTS ON PROPERTIES OF R-PET/HDPE BLENDS

SUMMARY

New properties and lower prices of polymers are needed to meet demands of the polymer industry and the requirements increase day by day. The polymerization process is a method which is preferred in the laboratory criteria by researcers. Unfortunately the demands for many applications can't be fulfilled by polymerizations polymers. Polymer blending is cheaper and easier method than the other producing polymers. Therefore blending method is most suitable for the new polymer application and their importance increases day by day.

The discovery of the polymer blending method is based on a very ancient years but academic and an industrial study of polymer blends were started at the end of 1960 and continued to increase. The most important reason is that being the examination of the two polymer miscibility and is done in many academic publications on this topic. As a result of studies conducted on the mixture of polymers is presented General Electric Noryl® commercial products on the market.

In the blending method, it is aimed that weak properties are repeared by addition of second polymer. However it is generally obtained with heterogeneous morphology when two polymers are mixed because of high molecular weight, different chemical structures and crystallinity.

Also blend morphology depend on several parameters like as screw speed, process temperature, amount of concentrations etc. Blend morphology is the most important parameter that determines the final product properties. Therefore the scope of this study, it was investigated that the most appropriate screw speed, amount of compatibilizer and concentration of R-PET affect on R-PET/HDPE blends.

This thesis aimed to study the low mechanical properties of High Density Polyethylene (HDPE) was mixed Recycled Polyethylene Terephthalate (R-PET) to obtained high mechanical properties. Also we aimed to increase the processebility of R-PET with the helping of HDPE. Ethylene Ethylacrylate Glycidyl Methacrylate Terpolymer (E-EA-GMA) was used a compatibilizer. First of all to see the effect of screw speed, the R-PET/HDPE/E-EA-GMA (30/67/3) blends were prepared at five different screw speed (5-8-10-12-15-18 Hertz). Then R-PET/HDPE blends were prepared at various R-PET compositions (10, 15, 20, 25, 30, 35, 40 and 50wt%) in a twin screw extruder. In addition R-PET/HDPE/E-EA-GMA compatibilized blends were prepared with 3%wt and 5% wt E-EA-GMA.

All process parameters were kept constant during the preparing all of blends. Then, the samples were moulded by using injection moulding machine for measuring of mechanical properties.

R-PET/HDPE/E-EA-GMA blends were examined by SEM, Fourier Transform Infrared Spectroscopy (FTIR) and universal test machine.

According to result of SEM analysis, the screw speed more than 10 Hertz caused gathering of R-PET droplets and decreasing of mechanical properties of R-PET/HDPE blends due to coarse morphology. Therefore all composition of prepared blends were blended at 10 Hertz screw speed.

First of all the Young Modulus of R-PET/HDPE blends were increased by concentration of R-PET without compatibilizer. On the other hand the increase of amount R-PET badly affected in tensile stress and impact strenght because of weak interaction between R-PET and HDPE polymers and poor extantion properties of R-PET. This weak interaction between polymers were examined by scanning electron microscopy (SEM) analysis. The two polymers are immiscible and need to be compatibilized in order to be used in commercial applications. So 3wt% and 5wt% E-EA-GMA were added in the blends to solve the problems. Addition of compatibilizer decreased the droplets size and interphase tension.

The result of study, optimal parameters were tried to determine for the blend can be used in pipe production

VİDA HIZI, UYUMLAŞTIRICI VE R-PET MİKTARININ R-PET/HDPE HARMAN ÖZELLİKLERİNE ETKİSİ

ÖZET

Polimerlerin endüstride kullanılmaya başlanması ile birlikte birden fazla özelliği aynı anda bünyesinde taşıyan polimerlere olan ihtiyaç günden güne artmıştır. Polimerizasyon yöntemi ile yeni bir polimer elde etmek laboratuvar ölçütünde tercih edilen bir yöntem olsa da daha ucuz ve kolay bir yöntem olan polimer harmanlama metodu polimer endüstrisinde kullanılan ve önemini gün geçtikçe arttıran bir yöntemdir.

Polimer harmanlama yönteminin keşfi çok eski yıllara dayansa da polimer harmanları ile ilgili yapılan akademik ve endüstüriyel çalışmalar 1960 yıllarının sonunda başlamış ve artarak devam etmiştir. Bunun birçok sebebi olmasının yanında en önemli sebebi iki polimerin karışabilirliğinin incelenmesi ve bu konu hakkında birçok akademik yayın yapılmasıdır. Polimerlerin karışımı konusunda yapılan çalışmalar sonucunda General Elektrik ilk olarak Noryl® isimli ticari ürünü piyasaya sunmuştur.

Harmanlama yönteminde, fiziksel olarak karıştırılan polimerlerin güçlü oldukları özellikler kaybettirilmeden, zayıf olduğu düşünülen özellikleri, eklenen diğer polimer yardımıyla arttırılması amaçlanmaktadır.

Bu nedenle bu çalışma kapsamında proses edilebilirliği yüksek fakat mekanik özellikleri bakımından zayıf yüksek yoğunluklu polietilen (HDPE), mekanik özellikleri yüksek ancak proses edilebilirliği oldukça düşük olan geri dönüşüm poli(etilenteraftelat) (R-PET) polimeri ile harmanlanarak yeni bir polimer harmanı eldesi amaçlanmıştır.

Yüksek molekül ağırlığına, farklı kristalinite ve kimyasal yapılara sahip polimerlerin harmanlanması sonucu genellikle heterojen morfolojiye sahip polimerler elde edilir. Ayrıca harman morfolojisi vida hızı, proses sıcaklığı, bileşen miktarı vb. birçok parametreye göre de değişiklik göstermektedir. Harman morfolojisi son ürün özelliklerini belirleyen en önemli parametredir. Bu nedenle çalışma kapsamında en uygun vida hızı, bileşen miktarı ve uyumlaştırıcının R-PET/HDPE harmanına olan etkisi incelenmiştir.

Çalışmada kapsamında, ilk olarak homojen bir morfoloji elde edebilmek amacı ile beş farklı (8-10-12-15-18Hertz) vida dönüş hızında harmanlar hazırlanmıştır. Daha sonra yapılacak tüm harmanlama çalışmalarında kullanılacak olan vida hızı bu şekilde seçilmiş ve diğer harmanlar için uygulanmıştır.

Çalışmanın ikinci kısmında ise farklı R-PET miktarlarına sahip (10-15-20-25-30-35-40-50wt%) R-PET/HDPE harmanları çift vidalı ekstrüder kullanılarak elde edilmiştir.

Farklı yapı ve kristaliniteye sahip R-PET ve HDPE polimerlerinin harmanlanması sonucu heterojen bir morfoloji elde edildiği yapılan literatür çalışması sonucu bilinmektedir.. Bu nedennle çalışmanın son kısmında farklı miktarlarda uyumlaştırıcı eklenerek, uyumlaştırıcının karışmayan harmanlara olan etkisi incelenmiştir. Bu amaçla 3wt% ve 5wt% Etilen-etilakrilat-Glisidil metaakrilat (E-EA-GMA)) uyumlaştırıcısı eklenerek morfolojik sonuçlara göre uyumlaştırıcı etkinliği belirlenmiştir.

Elde edilen tüm harmanların mekanik özelliklerinin incelenmesi için enjeksiyon prosesi ile kaşık ve darbe çubukları üretilmiştir. Mekanik testlerin sonuçlarının yorumlanabilmesi için harman morfolojisi SEM analizi ile uyumlaştırıcı etkinliği ise FTIR testleri yardımı ile incelenmiştir.

Farklı vida hızlarında hazırlanan harmanların morfolojik ve mekanik özellikleri incelendiğinde vida dönüş hızının R-PET damlacıklarının HDPE matrisi içerisinde dağılımına ve bununla beraber homojen morfoloji eldesinde önemli bir parametre olduğu sonucuna varılmıştır. SEM analizleri incelendiğinde 5 Hertz vida hızının R-PET damlacıklarının parçalanması için gerekli olan gücü sağlayamadığı görülmüştür. 8-10-12Hertz vida hızları homojen bir morfoloji sağlarken, vida hızının 15 ve 18'e çıkarılması ile birlikte damlacıklar yüksek kayma geriliminden dolayı tekrar birleşerek faz dönüşümüne neden olmuşlardır. Bu sonuç mekanik özellikleri olumsuz etkilemiştir.

Uyumlaştırıcı kullanılmadan hazırlanan R-PET/HDPE harmanının Young's modül değerlerinin R-PET miktarı arttıkça arttığı, çekme dayanımının ise iki polimer arasındaki geriliminden kaynaklı heterojen morfolojiden dolayı düştüğü SEM analizlerinden gözlenmiştir. R-PET ve HDPE polimerlerin karışmaz polimer olmalarından kaynaklan heterojen morfoloji %3 ve %5 oranında E-EA-GMA kopolimeri kullanılarak iyileştirilmeye çalışılmıştır. Uyumlaştırıcının eklenmesi ile dağınık faz damlacık boyutunun küçüldüğü ve bunun sonucu olarak daha homojen bir morfoloji elde edildiği SEM görüntüleri yardımı ile gözlenmiştir. Ayrıca homojen morfoloji daha yüksek çekme dayanımı eldesi sağlamıştır. Ancak uyumlaştırıcının elastik yapısı modül değerlerinin bir miktar düşmesine neden olmuştur.

Plastik boru sektörünü kendi içinde değerlendirdiğimizde polietilen (PE) ile üretilen bir borunun düşük mekanik özelliklerinden dolayı polivinilklorür (PVC) ile rekabette zorlandığı görülmektedir. (Polietilenin elastisite modulü, polivinilklorürden yaklaşık 3 kat daha düşüktür).

Plastik sektöründeki bu maliyet düşürme ve kalite yükseltme ihtiyacı nedeni ile kompozit ve harmanlama (birden fazla polimerin birbir ile karıştırılması-blend) teknolojileri gün geçtikçe önem kazanmakta, üreticiler çeşitli takviye malzemeleri ile ürünlerinin özelliklerini geliştirmektedir.

Örneğin, 1930 yılından itibaren otomobil uygulamalarında kullanılan nitril kauçuğunun havadaki ozon nedeni ile yıpranmasının önüne geçebilmek için ozona dayanıklı bir malzeme olan PVC ile harmanlanması daha uzun ömürlü malzeme eldesine neden olmuş ve bu yöntem dünyada geniş çapta uygulanmaya başlanmıştır. Benzer bir düşünce ile proje de plastik boru eldesinde kullanılan polietilenin düşük mekanik özelliklerinin daha nitelikli bir başka polimer ile geliştirerek daha rekabetçi ürünler elde edilmesi amaçlanmıştır. Genel olarak sektöre bakıldığında kimi üreticiler kompozit teknolojisini sadece maliyetleri düşürmek amacı ile matris hammaddesini yüksek oranlarda dolgu görevi gören mineraller ile karıştırmış ancak bunun sonrasında üründe başka kırılganlık olmak üzere pek çok kalite problemi

yaşamıştır. Bu nedenle kompozit ve harmanlama teknolojileri kullanılırken maliyetlerin dışında ürün performans kriterleri de göz önünde bulundurulmalıdır. Diğer yandan son zamanlarda artan çevre hassasiyeti ve özellikle Avrupa Birliği ülkelerinde getirilen yaptırımlar dikkate alınarak daha çevreci ürünler geliştirmek firmaların dikkat etmesi gereken bir başka noktadır.

Bu hususlar dikkate alınarak proje kapsamında yüksek yoğunluklu polietilenin mekanik özellikleri PET'in yüksek maliyeti ve çevreye olan negatif etkileri göz önüne alınarak geridönüşüm PET ile harmanlanarak arttırılmaya çalışılmıştır.

SAN-TEZ kapsamında toprak ve trafik yüküne maruz kalan ve mukavemetin çok daha fazla önem teşkil ettiği alt yapı boruları hedef ürün olarak seçilmiştir. Bu çalışma sonucunda farklı vida, R-PET ve uyumlaştırıcı miktarları denenerek hedef ürün için optimum parametreler belirlenmeye çalışılmıştır.

1. INTRODUCTION

Thermoplastic materials are relatively cheap, easy processing, lightweight materials with high resistance to chemicals and corrosion. However, compare with these, mechanical properties of thermoplastic polymer may be lower than the ceramic, metal or engineering resins and it is a problem for many applications that require strength. For example, even if the plastic pipe industry in itself considered, polyethylene pipes are forced to competition with polyvinylchloride (PVC) pipes due to the low mechanical features. Therefore, day by day composite and blending technologies are becoming increasingly important because of the need to both upgrade the quality and cost reduction to the plastics industry. A wider diversity of composite materials are produced by blending technology two or more commercially available polymers. However, the partners in most of the polymer blends are thermodynamically immiscible. Usually, the immiscible blends form a two-phase system. This two-phase has high tension and there isn't any chemical or physical bonding occur between interfaces. On account of the weak inter phase boundaries occur poor mechanical properties. To overcome these problems, functionalized polymers are used as compatabilizers that can minimize interfacial tension and improve adhesion between the two phases.

1.1 Purpose of Thesis

The aim of the thesis is that, High Density Polyetylene (PE) properties are developed by innovative, environmentally friendly and low cost methods and to obtain that using of this new material in a plastic industry. In the thesis, the blending technology will be used to instead of mineral fillers due to the quality problems of filler minerals. Therefore, HDPE will be blended with higher mechanical properties of other polymers than itself. Considering mechanical properties, environment and innovation factors, we decided to use of recycle polyethylene (terephthalate) (R-PET) is obtained from waste bottles as the reinforcement of the polymer. So that a new raw material may be possible used for the production of plastic pipe sector.

2. POLYMER BLENDS (LITERATURE SURVEY)

Polymer blends are physical mixtures of two or more polymers. There is no chemical bonding between them. Polymer blends are combinations of two polymers with one or more special properties that contribute to require for the proper functioning of a specific application. The modification of already existing polymers is more economically viable than the synthesize of new monomers for the production of new applications. In former years, numerous systems based on the chemical combination of different monomers through random, block, and graft copolymerization methods were produced in order to obtain a new product. However, implementation of this method was difficult and costly in the polymer industry. For similar reasons, the blending technology has been the focus of new studies nowadays, both theoretical and experimental [1]. For instance, the coating and rubber industries blended different low molecular weight polymers at first [2]; and the first polymer blend was patented in 1846 by Parkes.This blend of natural rubber with gutta-percha resulted in a partially crosslinked material whose modulus was controllable by the composition of each isomer [3]. Although noted to be of interest much earlier, the academic and industrial attention in polymer blends enduringly increased starting in the late 1960s.

The fact that there were many reasons responsible for this increase. The one significant factor was the emergence of a major engineering polymer blend based on polystyrene (specifically impact polystyrene) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Miscibility of these polymers has paved the way for new research topic and a lot of academic work has been published about miscibility continues to be published [3]. However,even if polymer blends is becoming a more and more interesting research area for industrial and academic point of view, we still do not have a clear understanding of the morphology evolution inimmiscible polymer blends. There is not yet a universal theory describing the evolution of morphology of immiscible phases systems [4].

Therefore, controlling the morphology of these blends are the key point of the future development of this type of materials. Currently, polymer alloys and blends comprise

over 80wt% of all plastics. In addition, the polymer blends segment of the plastics' industry increases at about three times faster than the whole plastics' industry. In polymer industry, polymer blends are becoming more important raw materials because they can frequently meet performance requirements that cannot be provide by the currently available commodity polymers. A continuous need for new materials is created by the increasing complexity of products that result from technological breakthroughs and the desire to obtain improved, cheaper materials for existing applications. By the year 2000 the world market for polymer blends is expected to reach 51 million tons per annum, worth well over US$ 200 billion [3].

Growing of blending technology reason is that providing attractive opportunities for reuse andrecycling of polymer wastes. Also the opportunity to develop or improve on properties to meet specific customer needs.

We can accomplished various economic and property advantages by blending are:

- The capability to reduce material cost with or without little sacrifice in properties
- Permit the much more rapid development of blending materials to meet emerging needs by by-passing the polymerization step
- Light weight
- The ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products
- Improved modulus, hardness, barrier property, flame retardant property, impact and environmental stress cracking resistance, etc [1].

Besides the advantages of the polymer blend, the balance and surface interaction behavior cause some of disadvantage. To overcome these problems, functionalized polymers are used as compatabilizers that can minimize interfacial tension and improve adhesion between the two phases. The results are a finely dispersed phase and improvement of the overall properties of the blends [5].

2.1 Polymer Blend Types

Polymer blends can be classified by the compatibility and homogenization of the system. When two polymers are physically mixed, two different phase structure can be occured. According to the phase structure of polymer blends are divided into two miscible and immiscible.

2.1.1 Miscible blends

The most important factor leading to miscibility in low molecular weight materials is the combinatorial entropy contribution, which is very large compared to high molecular weight polymers [6]. Complete miscibility in a mixture of two polymers requires that the following condition is fulfilled:

$$\Delta G=\Delta H - T\Delta S \quad (1.1)$$

where ΔGm, ΔHm, and ΔSm respectively are the Gibb's free energy, the enthalpy and entropy of mixing at temperature T.

(i) The free energy of mixing should be negative or zero

(ii) The second derivative of free energy function with respect to volume fraction of major component should be positive [1].

$\Delta Gm<0$

$$\left(\frac{\partial^2 \Delta G_m}{\partial \varphi_i^2}\right)_{T,P} > 0$$

Miscible polymer blends are homogeneous down to the molecular level and associated with the negative value of the free energy of mixing. The value of TΔSm is always positive because mixing increase entropy. Therefore, the sign of ΔGm always depends on the value of the enthalpy of mixing ΔHm. The polymer pairs mix to form a single phase only if the entropic contribution to free energy exceeds the enthalpic contribution, i.e

$\Delta Hm < T\Delta Sm$

For most polymer blends the miscibility rises with increasing the pressure. The effect depends on the magnitude of the heat of mixing ΔHm. For $\Delta Hm < 0$ the miscibility is enhanced by compression, whereas for those with $\Delta Hm > 0$ it is reduced [7].

In also miscible blends behave similarly, to what is expected of a single-phase system.Both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components [8]. For example in Figure 2.1, A single glass transition (Tg) polymer is formed when two miscible polymer mix.

Glass transition temperature is the average of the two of Tg's of polymers.

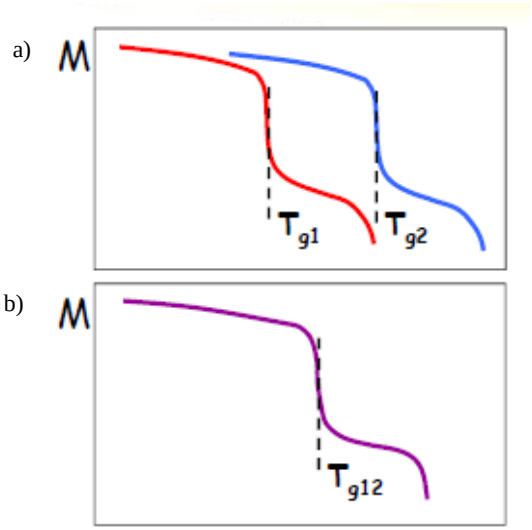

Figure 2.1: Tg of miscible polymer blends a) Pure components b) Miscible blend [9].

2.1.2 Immisible blends

Most mixtures of polymer blends are thermodynamically immiscible because of large molecular weights. Entropic contribution of large molecular weights to ΔGmix for polymer pairs are much smaller than low-molecular weight polymers and ΔHmix practically controls polymer blend of miscibility. This shows that the free Gibbs energy of mixture is positive for high molecular weights polymer [10]. These blends are referred to as immiscible blends. Immiscible polymer blends form a two-phase system (dispersed phase-matrix phase) which mostly show rough phase structure and poor interphase adhesion. On account of the weak inter phase boundaries produce poor mechanical properties. In such cases, it is generally assumed that either the sizes of the dispersed domains are not optimal or the immiscibility of the two phases produces weak interfaces, leading in turn to easy failure of the blend under stress.

For this reason, immiscible polymer couples seem difficult to use material application but; immiscible blends constitute most of the commercial blends. The main reason that, mixing miscible polymer lose their individual properties whereas blending of immiscible polymers are an economically attractive route to develop new materials that combine the desirable properties of more than one polymer [9]. The names of some immiscible blends and applications are given in Table 2.1.

Immiscible morphology generally create a coarse morphology which induce weak adhesion and low mechanical properties. To overcome weak interaction between polymers; functionalized polymers are used as compatabilizers that can minimize interfacial tension and improve.

Table 2.1: Some of commercial blends[10].

Commercial Name	Producer	Blends	Application area
FerroFlex	Ferro Corp.	PP/EPDM	Automotive, electricity
Hostadur X	Hoechst AG	PBT/PET GF	Computer
Gemax	G.E.	PPE/PBT	Automotive
Kydene	Rohm and Hass	PVC/PMMA	Thermoformable sheet
Orgalloy	Atochem	Nylon-6/PP	Automotive body
Saranex	Dow	PVDC/PE	Film
Mindel B	Amoco	PSO/PET GF (40%)	Thermal resistance

R-PET/HDPE blend which used in thesis is another example for immissible polymer blends. Different molecular structures, polarities and crystallization behaviors give immiscibility to them. The unfavorable interactions between the R-PET/PE molecular chains would lead to large interfacial tension in the blend morphology and make it difficult to disperse the components during extrusion.

Interfacial tension (κ) controls the adhesion of the two polymers. Due to interfacial adhesion is an important issue affecting the final product properties, there are several studies on interfacial tension. The interfacial tension is obtained in these studies are summarized in Table 2.2.

Table 2.2: Some of interfacial tensions of polymer blends [11].

Polymer	Polymer 2	Temperature (°C)	κ (dyne/cm2)
Polyethylene	Polystyrene	290	5.0
Polyethylene	Polysulfone	290	6.5
Polyethylene	Poly(p-phenylene sulfide)	290	7.2
Polyethylene	Poly(ethylene terephthalate)	290	9.2
Polyethylene	Poly(bisphenol A carbonate)	290	13.0
Polyethylene	Polyamide 6	290	13.2
Poly(p-phenylene sulfide)	Polysulfone	290	1.6
Poly(p-phenylene sulfide)	Polycarbonate	290	3.5
Poly(p-phenylene sulfide)	Polyamide 6	290	9.9

As shown in Table 2.2 interfacial tension value of PE and PET (9,2 dyne/cm^2) blends got higher value than many other immiscible blends (such as (poly p-phenylene sulfide, polikarbonat; (3,5dyne/cm^2)). Large interfacial tension can cause phase separation morphology. The morphology is improved by adding a third component as called compatibilizer.

2.2 Method of Polymer Blends Production

Phase morphology and interfacial bonding is influent to determine the properties of the product.Therefore, the production process of polymer blends are an extremely important process. Applications of polymer blends are produced by the method of mechanical mixing and melting. Mixing is performed with the extrusion, cylinders or kneading machines [12].

Among various types of mixing equipment, twin-screw extruders have most widely been used to prepare polymer blends in industry to provide a homogenous mixture. Polymers are mixed and pushed forward to die in extruder with the help of screw. The extrusion process is a continuous process, so that the time and working efficiency is provided.

In preparation of the polymer blend, firstly, extruder temperatureis adjusted to a temperature above the melting temperature of either polymer. However, it should be noted that, having a low melt temperature polymer isn't decomposed by the seting high temperature.Removal of impurities and moisture from polymers are given from the hopper to the extruder.

As shown in Figure 2.2 polymer blend melts and remove in the form of pasta from extruder head. Then, as-extruded blends quickly cooled for the pelletizing and granules are obtain from chrushers machine.

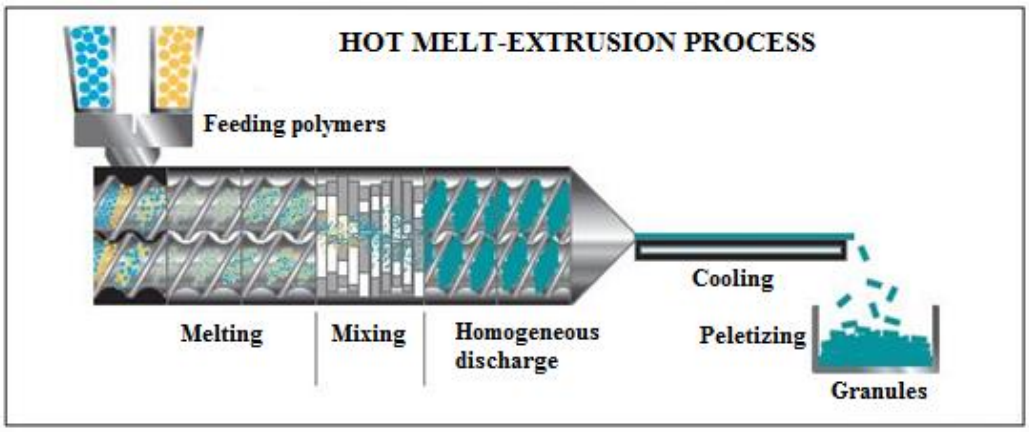

Figure 2.2: Extrusion process [13]

2.3 Properties of R-PET/HDPE Blends

PE elasticity properties are sufficient for textile applications,howover it is limited to using in other applications due to their low modulus and tensile strength. On the

other hand having high strength and modulus of R-PET are widely used in sectors such as packaging, synthetic fiber, film. R-PET has high values of strength and modulus but the process availability (workability) is low and a costly raw material all the same.Therefore, the second phase PE is selected to be blending with the R-PET polymer because of low cost and good processability.

Polyolefins compare to other engineering polymers, they are flexible, high workability and non-sensitive to moisture. On the other hand, PET has the unique mechanical and barrier features among the thermoplastic polymers. Besides, the result of blending of these two polymers polymer; moisture sensitivity of PET is reduced by hydrophobic nature of PE and PE plays an important role in crystallizingof PET. The modulus and tensile strength of the blend is proportional to the increase of the amount of PET. Heterogeneous morphology causing low mechanical properties are eliminated by the addition of compatibilizer [14].

According to academic studies about of PET / PE blends using different processes, it is proposed that the new products will be obtained in the future (Figure 2.3).

Forming methods	Applications	Melt Index (g/10min)	Required Properties
Extrusion		0.01~0.5 (high viscosity)	* High impact * High flexural modulus
Inflation Film		0.1~1	* Tensile elongation * Heat -sealing
Sheet		1~10	* Flexing strength * Heat-sealing
Fiber		10~30	* Tensile strength * Tensile elongation
Injection		10~50 (low viscosity)	* High impact * Dimensional Accuracy

Figure 2.3 Application area of PET/PE blends [15]

In addition to these applications, in A. P. Johari *et al* of study, PET/HDPE blends can also be used in these products; [16].

- Garden furniture
- Grass Pavers
- Flower pots
- Brush hair

- Shipping pallets
- Construction industry products
- Electronic products
- Heavy crates holding apparatus [16]

The scope of this thesis is that, the weak tensile strength properties of HDPE are improved by using R-PET. Because R-PET have high mechanical properties. On the other hand the having poor procesibility properties of R-PET is increased by HDPE. For this purpose, R-PET/HDPE blends were prepared by twin screw extruder. A random terpolymer was used as compatibilizer. Mechanical behavior and morphology of all blends were determined and the relationship between these two properties was investigated.

3. EFFECT OF PROCESS PARAMETRES ON R-PET/PE BLENDS

3.1 Effect of Morphology

A large part of the commercial blends consists of dispersed into droplets of reinforced polymer and matrix polymer. Apart from these droplets structure blends, there are fiber, layer (lamellar) and semi-continuous (co-continous) structure blends(Figure 3.1) [17]. According to the morphological structure; products show different properties such as strength, stiffness, barrier, toughness and melt flow.

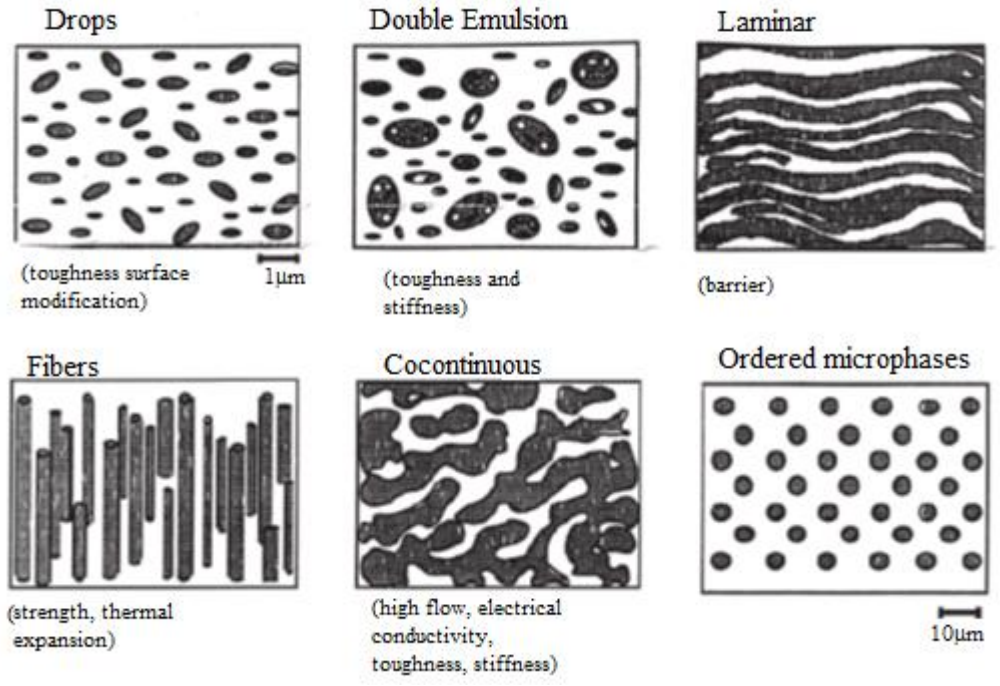

Figure 3.1 Morphology structure of polymer blends [18]

Basically, the two polymers are blended with the extrusion process, two different morphologies might be occurred [10]. The first of these, major phase initially melts which is formed the dispersed phase morphology. Minor phase melts after the matrix phase and disperses as droplets in the matrix phase.

In the second morphology; small amount of polymer prior to melt and its arround is wrapped by major phase polymer and phase conversion occurs.This type of morphology is called semi-continuous morphologies [12].

Extrusion process may seem like a very short and easy method, but during the process, mixture control is very importantand diffucult issue for the manufacture of new features as the material. It is difficult due to control of the morphology depends on many process parameter.

Amount of components, screw speed, temperature, residence time, cooling rate, interfacial tension and elastic properties of the components affects the phase structure. A single formula which including all these parameters hasn't been developed yet [19].

For this reason, to understand the effect of phase morphology, researchers keep on study about the attempt of blends.

For examples, L. A. Utracki studied the effect of cooling rate on the distribution of the reinforcement phase in the matrix phase. Also he observed that, the distributionof reinforcing polymer changed depending on the extruder screw speed at the same time [10].

In another study Puyvelde *et.*, barrier properties of PE / nylon blendswere examined at different process conditions. When the naylon molecules dispersedlike droplets (blue line),barrier properties decreased. On the other hand, when the naylon molecules dispersedlike a sheets (red line), the barrier properties concluded that increased (Figure 3.2) [9]. In the study, added more than 40% nylon reinforcing, both the barrier properties of the blend increased but this increase was caused by the amount of nylon.

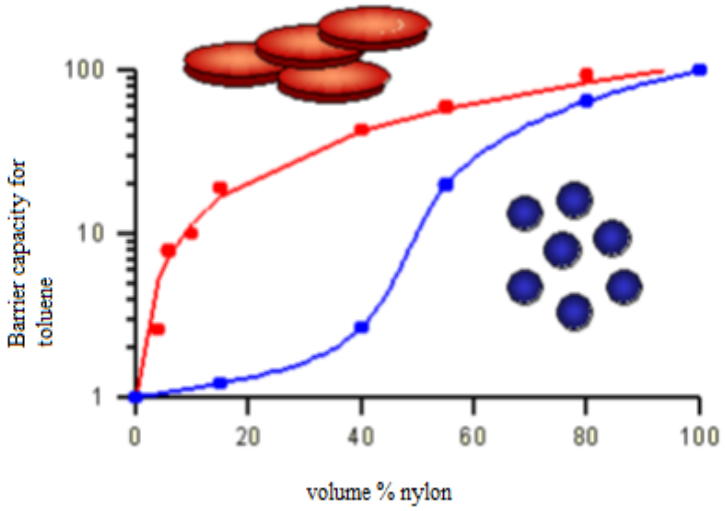

Figure 3.2: The effect of dispersed droplets on nylon barrier properties [9].

As a result, different from each other features of two products can be achieved with only changing the morphology.

3.2 Effect of the Compatibilizer

In industry, the most commonly used method toreduce the phase separation occurring in immiscible blends is that addition of a third component such as compatibilizers. These components may be block or graft copolymer of PET or PE. These types of components arepreviously synthesized and are added to the polymer blend during the process. These components are non-reactive, which localize in the interface of the polymer, besides reduce the interfacial tension and provides adhesion [9]. Compatibilizers reduce the interfacial tension,as well as provide to disperse homogeneous the reinforcing polymer of droplets in structure of blends.As seen from SEM images in Figure 3.3a;between PET and HDPE phase separation appears very sharply separated. On the other hand, in Figure 3.3b, this phase seperation has disappeared with the effect of compatibilizer[20].

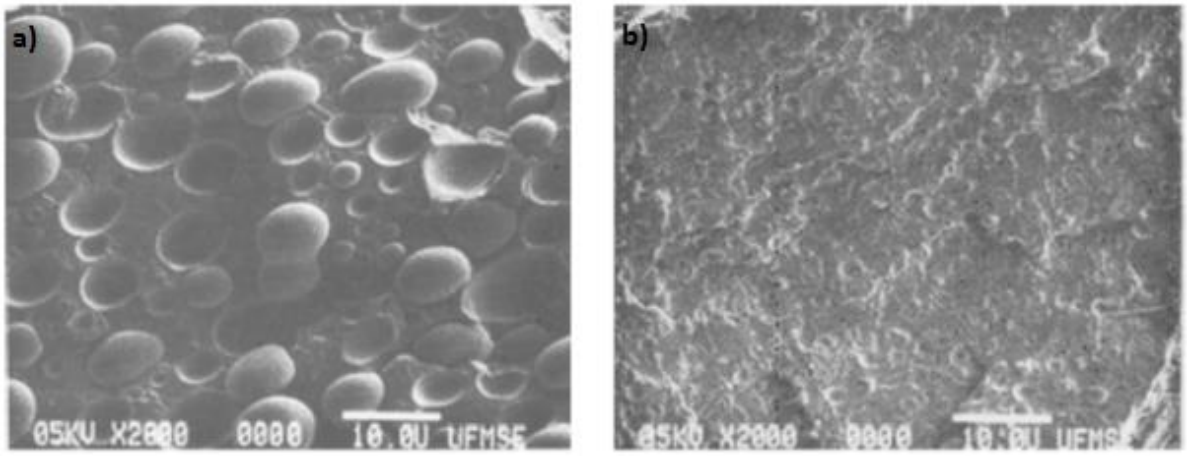

Figure 3.3:SEM fracture surface of blends with composition: a) HDPE/PET = 35/65,b) HDPE/grafted HDPE/PET = 30/5/65 [20]

In the literature, there are many studies on this subject. For example, in Table 3.1, White and Bummer summarize measured interfacial tension of PET-HDPE blend in different kinds of compatibilizer.

Table 3.1: Interfacial tensions of PET-HDPE blends [11].

Polymer 1	Polymer 2	Compatibilizer	Temperature (°C)	κ (din/cm^2)
PE	PET	-	270	9.7
PE	PET	PBT-b-PE copolymer	270	1.7
PE	PET	Maleated HDPE	270	1.9
PE	PET	SEBS	270	7.5
PE	PET	Maleated SEBS	270	1.8

As shown in Table 3.1, all added compatibilizers to the blend of PET-HDPE interfacial tension hasreduced [12]. In the study It is explained that maleic containing of compatibilizers reacted with end grup of PET which were found to be more effective than the other compatibilizer types.

Jabarin *et al*, they used styrene-ethylene / butylene-styrene (SEBS)as compatibilizer in PET/PE blends in their study. As a result of study, morphology of blends were homogeneous due to the structure of PET and SEBS were similar and end grup of PE connected with the styrene grup of SEBS [21].

Mariano *et al* examinated that, different types of compatibilizers affected on the mechanical properties of blends and the highest modulus was obtained by E-GMA of compatibilizer kinds. In addition, by adding 10 pph compatibilizer in the blend (matrix R-PE), the elongation at break increased 250%. According to the results of the impact test (as shown in Figure 3.4 for addition of 5 and 10 ppm% compatibilizer), it can be relized that, impact resistance was raised by addition of 10ppm% compatibilizer (SEBS-g-MA and E-GMA)[22].

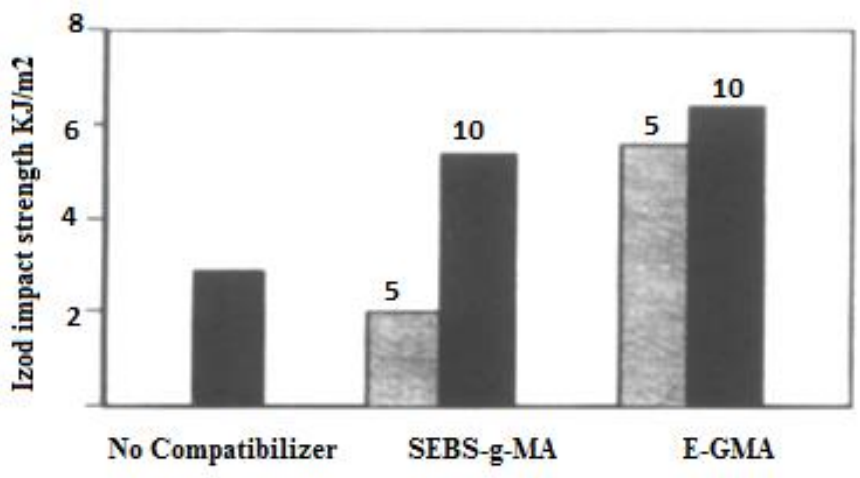

Figure 3.4: The graph of impact strength of R-PET/R-PE blends[22]

Kalfoglou *et al* used many types of compatibilizersuch as E-GMA, ethylene ethylacrylate glycidyl methacrylate terpolymer (E-EA-GMA), hydrogenated styrene-butadiene-styrene copolymer grafted with maleic anhydride (SEBS-g-MA), MA-modified ethylene-methyl acrylate copolymer (E-MeA-g-MA) and explored to affect of types of compatibilizer on the mechanical properties. By providing the best mechanical properties of compatibilizer is emphasized in the following ranking.

E-GMA > E-EA-GMA > SEBS-g-MA > E-MeA-g-MA [23].

Pluta added two types of compatibilizer (3%E-GMA or 5% SEBS) in the R-PET/R-PE (75/25) blend. When two types of compatibilizer compared, results supported by the of Kalfoglou is study. It was observed that 3% E-GMA caused the finner morphology on the immiscible blends. The most important reason of finner morphology is that SEBS-g-MA maleic anhydride groups reactonly with hydroxyl groups of PET. On the other hand, glycidyl methacrylate group of EGMA react with both hydroxyl and carboxyl group of the PET, and provided good adhesion between of two interfaces[24].

Compatibilizer amount is an important parameter, which affect on morphology as well as types of compatibilizer. In other study of Yao and Charles examined effect of amount of compatibilizer on the mechanical properties [20] (Table 3.2).

Table 3.2: Different amount of compatibilizer effect on the mechanical properties of PET/HDPE (50/50) blends [20].

Grafted HDPE %wt	Breaking Strength (%)	Izod Impact (ft-lb	Flexural Modulus (Kpsi)
Control	13.22	0.4	241.8
10	24.40	0.8	252.9
15	30.87	1.5	254.8
20	35.55	2.3	271.8
25	38.17	3.8	274.6
30	32.53	4.2	284.5

They used five different amount of compatibilizer. Acording to their observations, breaking strenght, izod impact and flexural modulus of all samples including control group increased until amount of compatibilizer reaches the optimum point at 25 % [20].

Pracella *et al*. determined to the best amount of compatibilizer using different amounts (1-5ppm) of EGMA. It was observed that non-compatibilized blend had fairly low elongation at break, when compared with individual breaking extension of pure R-PE (> 500) and R-PET (> 400). However, addition of 2-4 ppm E-GMA enhanced the elongation at break (110-370%) and tensile stress (until 19MPa to 23 MPa). Another conclusion drawn from this article is that the addition of a small amount of E-GMA had better mechanical properties than higher ratio the addition of SEBS-g-MA and HDPE-g-MA. This result is clue for determining the type of compatibilizer for low-cost production of blends[29].

An article of Pracella *et al.* was examined different morphologies due to observe different compatibilizer effect. SEM micrographs of copatibilized blends were shown inFigure 3.5. Due to the combination of droplets, a large dispersed phase could be seen in Figure 3.5a. The average radius of the large dispersed phase is 5μm. When 5% and 10% E-GMA were added, their average radius frequency decreased until 2.8 and 0.5 μm [25]. Dispersed phase particle size shrunk, increasing the surface area betweeninterface to reduce the surface tension and provides a good mixing.

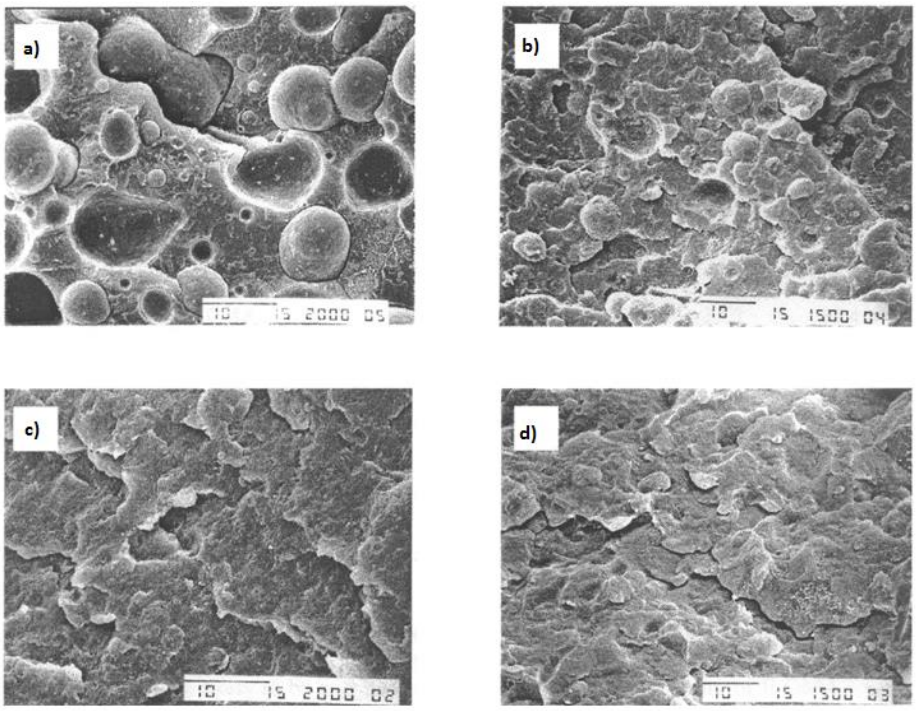

Figure 3.5: Blends of R-PET/HDPE (75/25) a) non-compatibilized b)E-GMA (%5)c) E-GMA(%10)d) SEBS-g-MA (%5) [26].

In the continuation of the same study of Pracella *et al*; E-GMA was found to be the most effective compatibilizer due to the effect of particle size [25-26].

There are many reasons for this. Such as;

- Group glycidylmethacrylate of E-GMA reacting with the OH of the request is stronger than maleic anhydride of HDPE-g- MA.
- E-GMA reacts with both groups OH and COOH of PET, on the otherhand, MA only react with group OH of PET.
- Esterification reactions are recyclableat high temperature.

In another study, it was observed that, compatibilizer prevented to merger of the droplets and it provided to homogeneously disperse to small particles in the matrix

phase [24]. Figure 3.6 shows the effect of different kinds of compatibilizer on particle size.

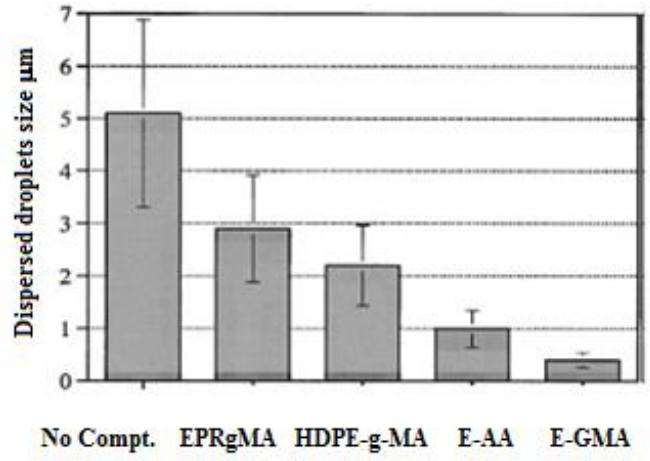

Figure3.6 Effect of different kinds of compatibilizer on avarege particle size at R-PET/HDPE (75/25) blends [24].

Pawlak *et al* used two kind of HDPE such as recycle (Ekogeminex) and pure (Rila A) who prepared compatibilized and non-compatibilized blends and according to the changing of amount of PET and mechanical properties of all blends determined (Figure 3.7) [27].

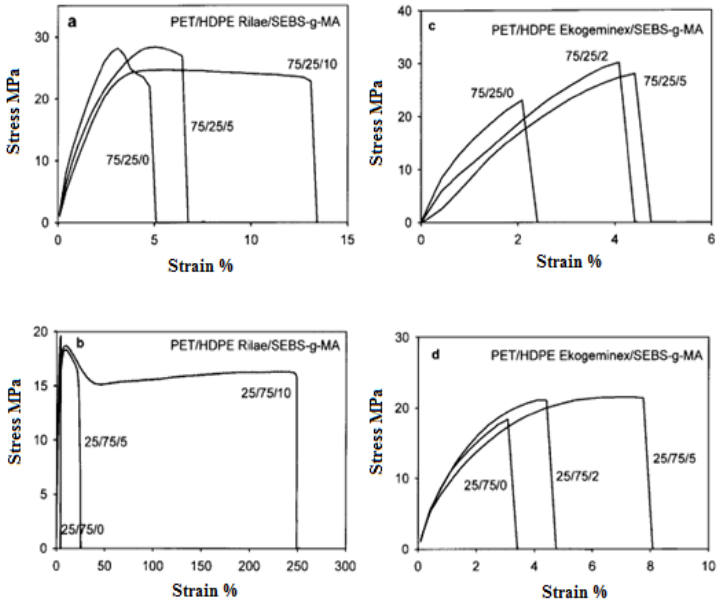

Figure 3.7 Mechanical properties of PET / HDPE / SEBS-g-MA blends [27].

The mechanical properies of blends prepared by using Ekogeminex were low compared to that of blends prepared using Rila A. The reason is that Ekogeminex is a recycling material and the structure of these foreign substances in recycle HDPE migrated toward the PET phase. Impurities disrupted structure of PET and caused to

reducemechanical properties due to hydrolysis of PET. It was observed that adding compatibilizer proveded a noticeable increase in the mechanical properties. With increasing of compatibilizer (SEBS-*g*-MA) elevated elongation at break and strength.Rich blend of HDPE plastic deformation is easier than the other blend. HDPE-rich blend of tensile strength was 19 MPa and elongation at break was 250% after having neck respectively.These values were higher than non-compatibilized and recycled blends (Figure 3.7)

Into the next part of the study, the same components were used but only compatibilizer has been changed to E-GMA. Mechanical properties have increased with the addition of E-GMA in Figure 3.8. The elongation at break for PET-rich blends increased 10-12%. Adding of 10ppm amount of E-GMA, tensile stress is increased from 27 MPa to 40 MPa. It was observed that HDPE-rich blend was quite ductile. Adding of 5 ppm amount of E-GMA, the elongation at break increased 60%. It was observed that the addition of E-GMA to PET/HDPE blends caused more increse in mechanical properties when compared to the SEBS-g-MA.

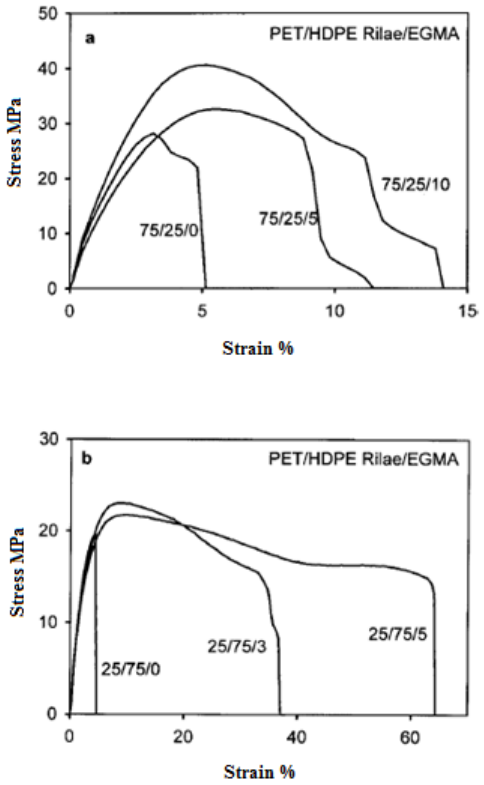

Figure 3.8: Mechanical properties of PET/HDPE/EGMA blends[27].

Impact resisitance of non-compatibilized blends were lower than compatibilized blends. (PET: 4,1 kJ/m2; HDPE:19,3 kJ/m2). To include 5wt% of SEBS-g-MA was not enough to increase impact resistance of PET / HDPE (75/25) blend. When increasing of compatibilizer content (10%), the impact resistance elevated have been seen. According to non- compatibilized blends, impact strength of compatibilized blends increased about 3.5 times (Figure 3.9).

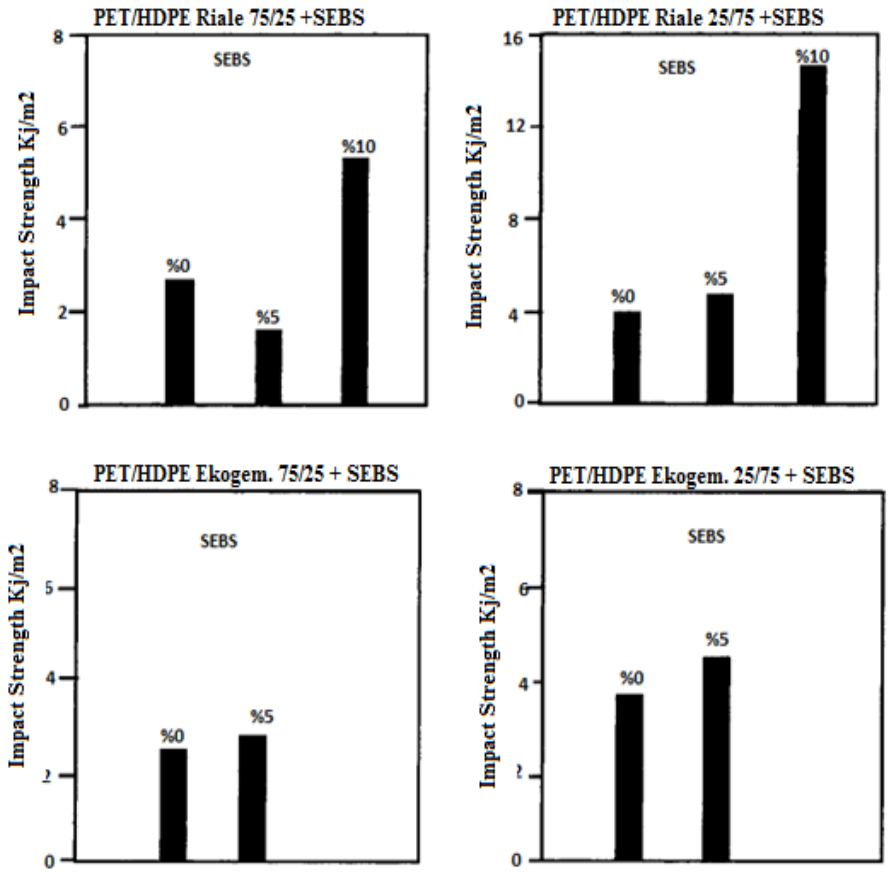

Figure 3.9 Impact test of PET/HDPE blends [27].

Consequently, using of compatibilizer eliminate phase separation of morphology and enhance mechanical properties.

3.3 Effect of Concentration Components

The amounts of the blend polymer comprising directly affects the morphology development. During blending of reinforcement and matris polymer, a sufficient concentration oflower melting polymer melts first. It surrounds dispersed phase, which constitutes matris phase. At the high process temperature, minor phase is dispersed in the matrix phase as droplets.By increasing the amount of reinforcing

polymer, phase conversion occurs and HDPE constitutes dispersed phase in addition PET constitutes matrix phase [28].

Effect of different amount of PET on PET/PE blends was examined by Chareunkvun [28]. Figure 3.10 presented the morphology of different amounts of PET/PE blends.

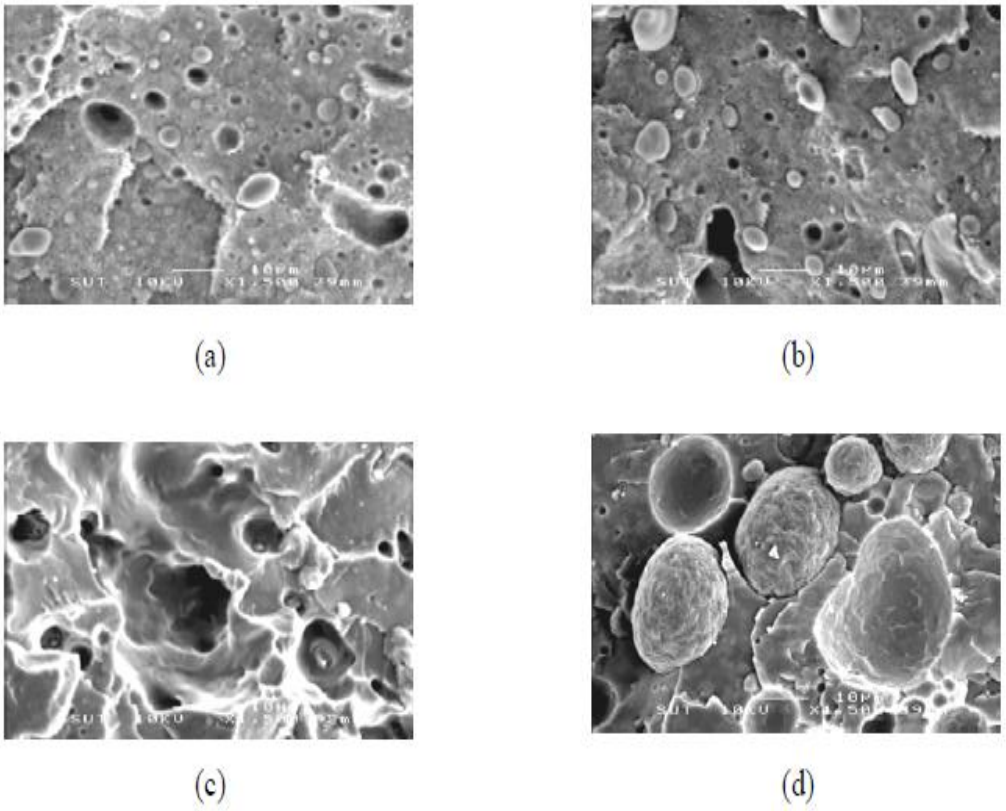

Figure 3.10 a)HDPE/PET 80/20, b)HDPE/PET 60/40,c)HDPE/PET 40/60 ve d)HDPE/PET 20/80[28]

It can be seen from Figure 3.10, dispersed phase morphology of HDPE-rich blend(Fig. 3.10a) is more homogeneous than PET-rich blend(Fig. 3.10d). The most important reason is the viscosity of HDPE is higher than the viscosity of PET.

Pawlak *et al.* prepared different amount of PET blends. They reported the effect of amount of reinforcement on the morphology. It could be seen that, HDPE acted as the reinforcing polymer in the PET-rich blend and dispersed in the form of drops in the PET matrix. HDPE drop size was measured 10–15 μm. However, the adhesion of between drops and the matrix phase appeared extremely poor. The size of the dispersed phase can be minimized by the addition of compatibilizer (5μm) and the weak adhesion could be increased. Reinforcement phase was PET polymer in the HDPE-rich (PET/HDPE (25/75)) blend and PET was distributed to form of droplets

in HDPE phase. The sizes of PET droplets were 3-5μm around. HDPE-rich blend was more homogeneous morphology than PET-rich blend but it is still quite poor adhesion between the phases [27].

The addition of SEBS-g-MA to blend eliminated phase seperation and reduced droplet size to 1μm.

Another effect is that amount of high strength PET increases, the modulus of blend increases. For example Chareunkvun reported that significant improvement in the young modulus and tensile strength of PET/HDPE blends when amount of PET was elevated (Table 3.3) [29].

Table 3.3: Mechanical properties od PET/HDPE blends [29].

Content (%Wt)	Tensile			Flaxural		Impact Strength (J/m^2)
	Strength (MPa)	Modulus (MPa)	Break Strength (%)	Strength(MPa)	Modulus (MPa)	
HDPE	18.10	731.6	-	24.1	805.96	20241.12
HDPE/ PET (80/20)	20.37	872.2	10.87	30.02	945.76	5763.29
HDPE/PET (60/40)	22.66	1007.8	4.04	35.58	1211.8	2928.71
HDPE/PET (40/60)	20.19	1146.7	2.44	31.78	1427.76	1685.55
HDPE/PET (20/80)	30.85	1320.7	3.46	54.49	1872.5	2578.41
PET	56.98	1663.5	4.42	89.92	2789.27	1435.42

Although the tensile strength is increased by increasing the amount of PET but PET cost is very high, increasing of R-PET is not a good methods for industrial applications. The blending of technology is the most important priority of economic studies for materials that can be achieved with a minimum amount of PET material high mechanical strength is desirable.

3.4 Effect of Screw Speed

The screw is a key component of extrusion process. Conveying of solids, melting homojenously and pumping of the polymer through the die are main functions of screw.

During the extrusion process, morfology of forming reinforcement polymer (B) and matrix polymer (A) are shown in Figure 3.11.

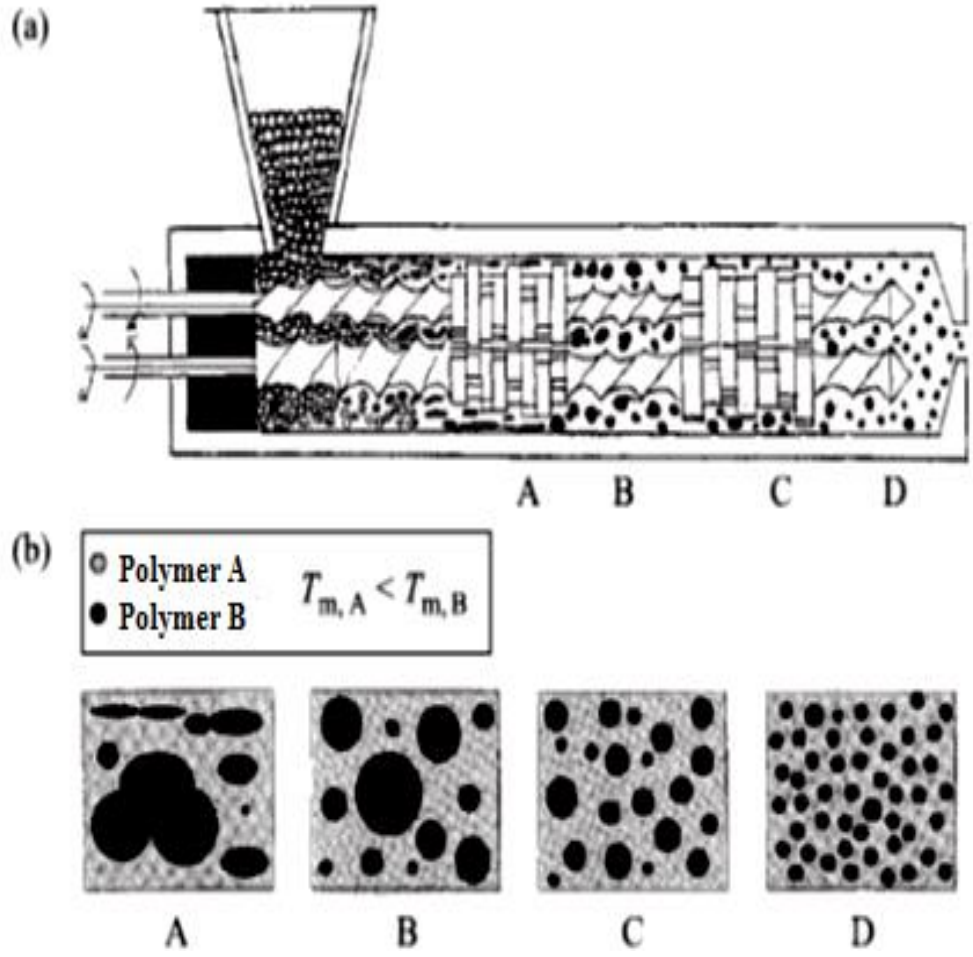

Figure 3.11 Forming of droplets during extrusion process[30]

The last product features are affeted by shape of the droplets as well as the droplet size is also an important contribution on product features.

Droplet size is determined with the interaction of surface tension of polymer and shear stress due to the rotation of the screw. As shown in the Figure 3.11, after the polymer blend is fed into the extruder, the reinforcement of polymer is dispersed as droplets in matrix phase depending on the screw speed. The size of these droplets depends on the screw speed.

Pawlak *et al*. have investigated the effect of screw speed on mechanical properties. They prepared PET/HDPE/SEBS-g-MA (75/25/5)-(25/75/5) blends in two different screw speed (500- 250 rpm) and examined relationship between the screw and mechanical properties of blends [27].

As seen in Figure 3.12, when the screw speed increased from 250 rpm to 500 rpm (sample of the residence time within the extruder is reduced), the elongation at break of both all blends reduced and yield strength increased.

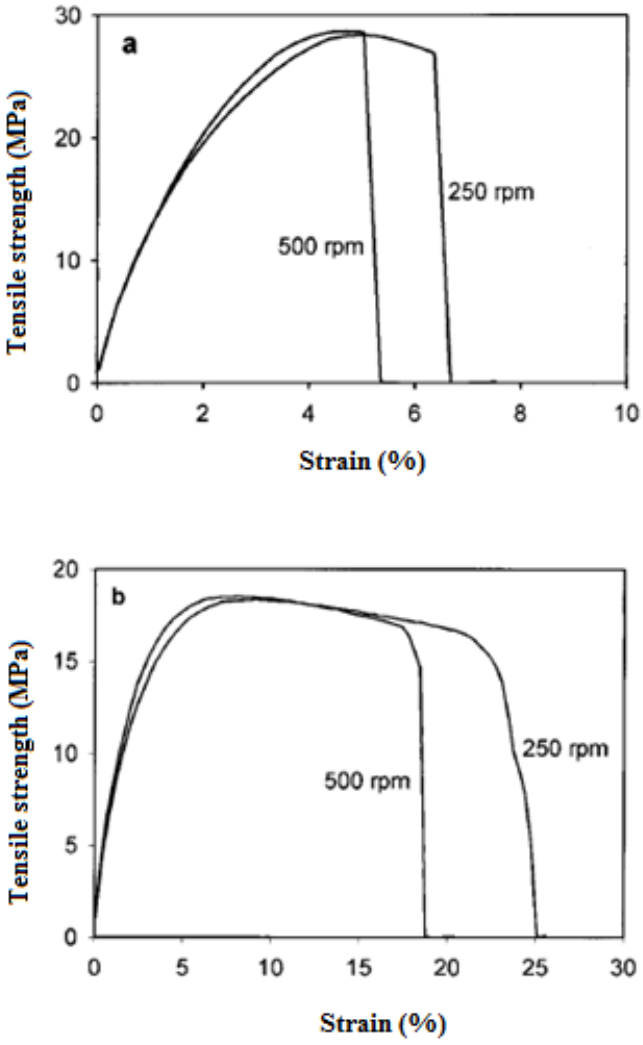

Figure 3.12: Effect of screw speed on PET/HDPE blends a)75 wt %/25 wt %/5 PET/HDPE Rilae/SEBS-*g*-MA b) 25 wt %/75 wt %/5 pph PET/HDPE Rilae/SEBS-*g*-MA [27].

In that case, another parameter to be considered is screw configuration, which was selected according to the polymer features. It should not be forgotten that just the right selected screw configuration obtains the desired homogeneous morphology and structure blends.

4. CHARACTERIZATION METHODS OF POLYMER BLENDS

The development of modern technology, performance of polymer blends has gained importance. Thus, performance of polymer blends are determined by many of the analysis methods and the highest features blends are trying to product.In this section, the most commonly used methods for the characterization of the blends will be informed about.

4.1 SEM Analysis

The fracture surfaces of the extrudates (strands) and injection molded (orcompression molded) samples were inspected using a scanning electron microscope (SEM). It is possible to observe the distribution of droplets, effect of compatibilizer, whether PET- HDPE polymers are mixed or not and adhesion between two phase by SEM.

4.2 Melt Flow Index Analysis

Compatibilizing effect is analyzed by (MFI) test. According to the results of MFI, we can be selected most appropriate type of compatibilizer. For example, it was observed from the litreture that the good adhesion of interfacial is obtained at low value of MFI (Figure 4.1).

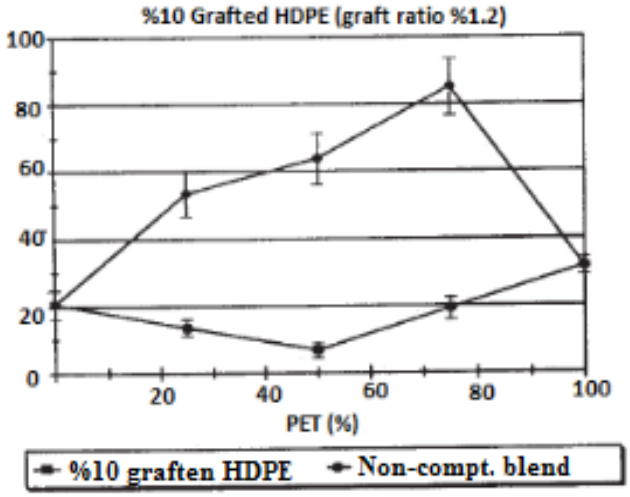

Figure 4.1: MFI value of non-compatibilized and compatibilized blends [20]

Compatibilizer, which yields the lowest MFI can be determined in this way. Li Yao *et al*., were observed that MFI value of compatibilized blends showed a sharp decrease after reaction occurred between polymer and compatibilizer (Fig. 4.1). This reduction is interpreted as; adding compatibilizer caused the viscosity increaseresulting from the process of the formation of new cross-links [20].

Pawlak *et al*. prepared blends in different molecular weight, different types and amounts. They investigated effectiveness of compatibilizer by MFI test. It was observed that there were quite large differences between their MFI value of non-compatibilized and compatibilized blends (Table 4.1).

Table 4.1MFI values of different type and amount of compatibilizer [20].

MFI (265 °C, 2.16kg)		
Sample	**Content %wt**	**MFI (g/10min)**
PET	100	25.3
PET (after extrusion)	100	44.4
HDPE Rilae	100	0.6
HDPE Rilae	100	0.2
HDPE Ekogeminex	100	0.8
HDPE Ekogeminex	100	0.2a
EGMA	100	10.3
PET/HDPE Rilae	75/25/0	31.0
PET/HDPE Rilae/SEBS-g-MA	75/25/5	26.6
PET/HDPE Rilae/SEBS-g-MA	75/25/10	16.5
PET/HDPE Rilae/EGMA	75/25/5	5.5
PET/HDPE Rilae/EGMA	75/25/10	7.5
PET/HDPE Rilae/HDPE-G-MA	75/25/10	20.2
PET/HDPE Ekogeminex	75/25/0	50.1
PET/HDPE Ekogeminex/SEBS-G-MA	75/25/2	26.1
PET/HDPE Ekogeminex/SEBS-G-MA	75/25/5	27.0
PET/HDPE Rilae	25/75/0	1.4
PET/HDPE Rilae/SEBS-g-MA	25/75/5	1.0
PET/HDPE Rilae/SEBS-g-MA	25/75/10	0.8
PET/HDPE Rilae/EGMA	25/75/10	0.8
PET/HDPE Rilae/EGMA	25/75/3	0.3
PET/HDPE Rilae/EGMA	25/75/5	0.3
PET/HDPE Rilae/HDPE-G-MA	25/75/10	0.8
PET/HDPE Ekogeminex	25/75/0	3.4
PET/HDPE Ekogeminex/SEBS-G-MA	25/75/2	2.3
PET/HDPE Ekogeminex/SEBS-G-MA	25/75/5	1.2

Their results showed that MFI value of blends was not only depent upon using compatibilizer, but also upon the type of compatilizer and its amount. According to recearchers, efficiency of one compatilibizer is measured by decreasing MFI values.

By taking into these point, amoung of compatibilizers E-GMA gave most effective results compare to HDPE-g-MA and SEBS-g-MA. [27].

4.3 FTIR Analysis

Fourier Transforms Infrared Spectroscopy (FTIR) spectrum is used in the structural analysis of the blends. Consisting of triple components in blending, the expansion the carboxyl group of PET is 1725 cm^{-1}. This value proves the presence of PET in the blend. The expansion band at low frequencies, it is an indication of the existence of the carbonyl group of PET [20]. Reaction between compatibilizer and the functional groups of PET is detected by using FTIR which provides that the adhesion between the two immiscible polymers. There are so many examples about using FTIR method in the literature.

Guerrero *et al* [31] used a compatibilizer, which is called commercial Surlyn resins in PET/HDPE blend, and they analyzed interactions of carbonyl group of PET and carboxylic acid groups of Surlyn structure using FTIR test method (in Figure 4.2).

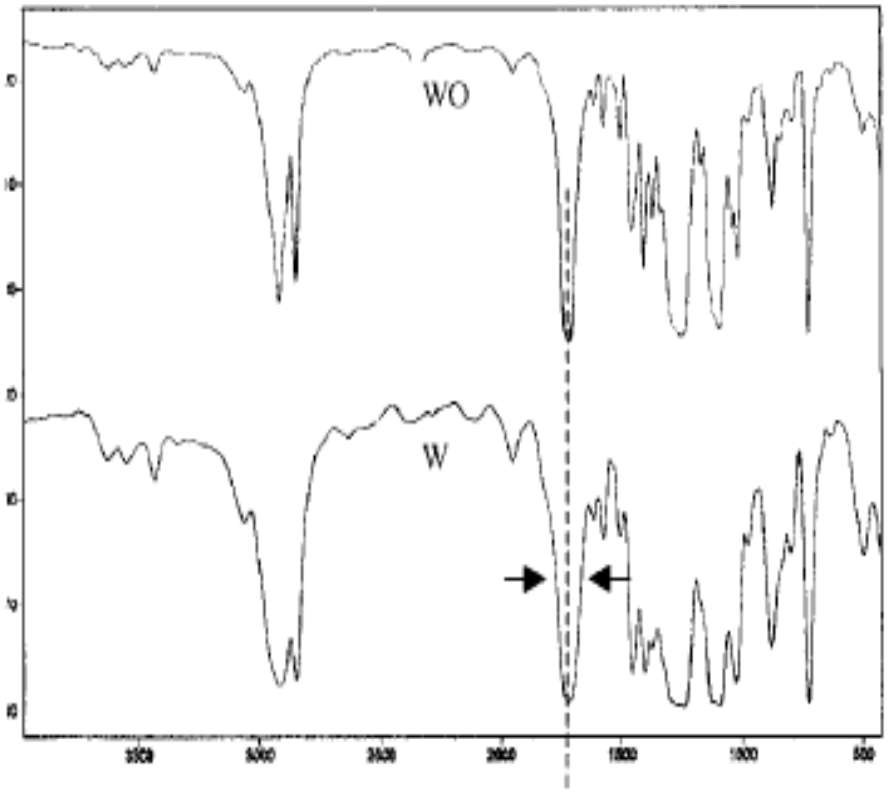

Figure 4.2 PET/HDPE (75/25) blends. WO=Non-compatibilized W= Compatibilized [31].

According to their analysis, addition of Surlyn caused that 1725cm^{-1} carbonyl band of PET was expanded because of reacting strong links between hydrogen bonds and carboxylic acid linkages. This proves that the harmonization of the blends.

Lee *et al* characterized R-PET and R-PE polymer of blends by FTIR at 1500–3000 cm^{-1} regions. They used different compatibilizers such as SEBS, MDI and PE-g-MA in the R-PET/R-PE to determine effect of compatibilizer. CH tension peak of R-PE at 2.917- 2.849 cm^{-1} and C=O tension peak of R-PET at 1.717 cm^{-1} were observed. Addition of 4,4- methylene-di-(phenyl isocyanate) (MDI) caused to disappear peak of 1791-1792 cm^{-1} (anhydride C = O peak voltage) and 2270 cm^{-1} (N=C=O voltage peak) [32]. This result provides evidence that, this anhydride and isocyanate groups were completely reacted with compatibilizer such as SEBS, PE-g-MA ve MDI. The activity of compatibilizers was analyzed by FTIR, the peak of R-PET/R-HDPE is showed in Figure 4.3.

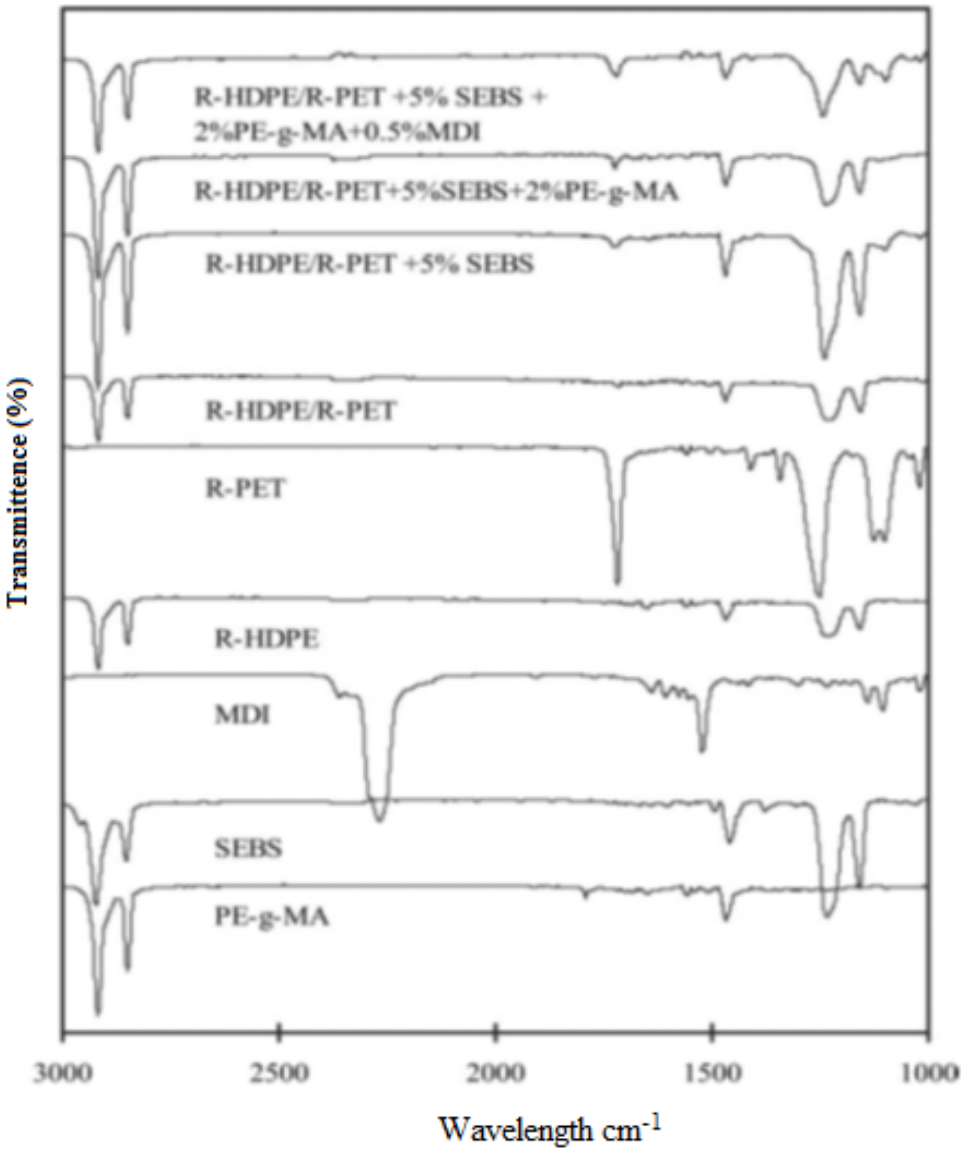

Figure 4.3: FTIR of R-HDPE/RPET (70/30 wt %) blends [32].

4.4 DSC Analysis

Crystallization and melting behavior of the blends are examined by differential scanning calorimetry (DSC) By changing the type and amount of compatibilizer, shift of the peak is observed. The data for pure PET and PET / HDPE blends are given in Table 4.2 and Figure 4.4. Without adding compatibilizer there was no shift of crystallization temperature of PET (184C°). After addition of compatibilizer crystallization temperature of PET changed. This is evidence the formation of strong interactions between copolymer and PET [27].

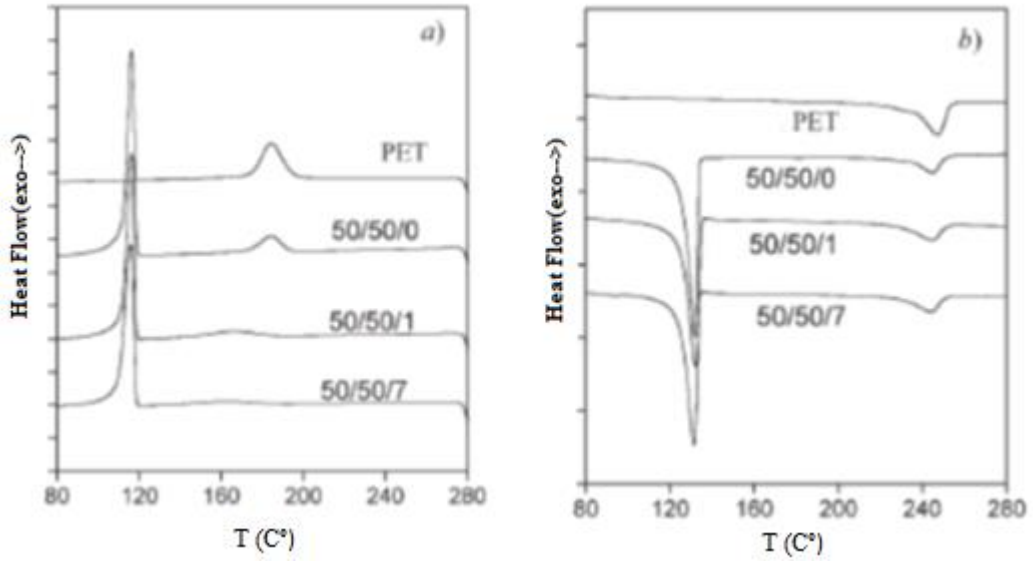

Figure 4.4 DSC analysisPET/HDPE –EMA blends a)Cooling b)Heating [28].

Table 4.2 DSC analysis of PET/HDPE/EMA [28].

Polymer	**Cooling**		**2. Heatig**		
	Tc (°C)	ΔHc (°C)	Tm (°C)	ΔHm (J/g))	Xc(%)
PET	184	38,5	247	36,5	30,4
50/50/0	184	36,1	245	37,6	31,3
50/50/1	161	20,5	244,4	37,7	31,4
50/50/7	160	-	244	38,6	32,2

Jarukumjorn and Chareunkvun examined about of PET and HDPE crystallinity. Also they observed that with the addition of compatibilizer, crystallinity of two components (PET and PE) decreased because of an increased interference adhesion [33]. They added different amount of compotibilizer in the HDPE/PET blends and they measured their crystallization degree. Some crystallization degree of HDPE / PET (75/25) blend result can be seen in Table 4.3. By Additing of PE-g-MA and increasing amount of PE-g-MA, the crystallization percentage (Xc%) decreased from

45.13 (HDPE/PET- 75/15) to 34.18 (HDPE/PET/PE-g-MA 75/25/10). The Xc reduction occurred because of reacting the tip of the reactive HDPE and hydroxyl-carboxyl group of PET. According to the views of Jabari and Bhakkad, locating of compatibilizer between two polymers reduced to Xc [34].

Table 4.3 The value of Tm and Xc non-compatibilized and compatibilized blends[34].

Sample	**HDPE**		**PET**	
	Tm (°C)	**Xc(%)**	**Tm (°C)**	**Xc(%)**
HDPE	133,3	62,39	246,77	-
PET	-	-	248,9	21,87
HDPE/PET/25/75	132,9	14,04	248,43	20,69
HDPE/PET/PE-g-MA 25/75/2	132,67	12,18	248,91	18,22
HDPE/PET/PE-g-MA 25/75/5	132,44	13,87	248,64	15,4
HDPE/PET/PE-g-MA 25/75/7	131,69	12,17	248,59	6,6
HDPE/PET/PE-g-MA 25/75/10	133,11	11,02	248,52	5,62
HDPE/PET75/25	132,69	45,13	246,65	4,04
HDPE/PET/PE-g-MA 75/25/2	132,69	41,79	246,65	2,95
HDPE/PET/PE-g-MA 75/25/5	132,37	40,25	246,1	3,44
HDPE/PET/PE-g-MA 75/25/7	132,61	39,2	248,29	3,3
HDPE/PET/PE-g-MA 75/25/10	133,3	34,18	248,6	3,31

5. EXPERIMENTAL

5.1 Materials

The materials used in this work which were recycle polyethylene terephthalate (R-PET), Bottle Grade PET Granule, Intrinsic Viscosity=0.72 – 0.82 dl/g) and high-density polyethylene (HDPE, Taixos, Formosa Plastic Corparation, Taipei,Taiwan). Compatibilizer is used random terpolymer of ethylene, methyl acrylate and glycidyl methacrylate (E-EA-GMA), Lotader AX 8900, from Atochem Co. France). The content of glycidyl methacrylate content in the E-EA-GMA copolymer is 8 mol % and methyl acrylate content in the E-EA-GMA copolymer is 24 mol %. Their properties, are summarized in Table 5.1.

Table 5.1 Raw materials used in the thesis

Characteristics	**PET**	**HDPE**	**E-EA-GMA**
Melt Flow Rate (MFR) (g/10 min) (190 °C,) Load (2,16kg)	-	1,0	6
Melt Temperature (°C)	249	134	60
Intrinsic Viscosity (dl/g)	0.72 – 0.82	-	
Density (kg/m^3)	-	949	950

* The data are taken directly from the data sheets of the manufacturers sites.

5.2 Preparation of HDPE/PET Blends

R-PET/HDPE blending process was carried out using a twin-screw extruder (Xında compounding system, L/D=48, Barrel diameter=35mm) with a temperature profile:90-235-245-260-265-270-270 and 260°C from hopper to die. The temperature profile was selected to ensure the minimum degradation of the components. The limit temperature was choosen as 270 which is 20°C higher than the melting temperature of R-PET. Before blending, R-PET was dried for 4 hour 100 °C to get rid of the moisture. Three parameters screw speed of extruder, R-PET concentration and compatibilizer amount were investigated in this study. A screw rotation speed of 5,8,10,12,15 and 18 Hertz were used ensuring the best homogenized blends for the R-PET/HDPE blends with 3wt% E-EA-GMA. The

blends of R-PET/HDPE at various compositions of 10/90, 15/85, 20/80, 25/75, 30/70, 35/65, 40/60 and 50/50 wt% were experienced at constant screw speed. E-EA-GMA was added in the R-PET/HDPE blends as compatibilizer at 3 and 5 wt%. Table 5.2 shows the preparing of blends in the study.

Table 5.2 List of blends prepared (wt %)

Sample code B-a/b/c-d	R-PET wt% Const.	Compatibilizer percentage (w%)	Screw speed ratio
B-10/90/0-10	10	0	10
B-15/85/0/10	15	0	10
B-20/80/0/10	20	0	10
B-25/75/0/10	25	0	10
B-30/70/0/10	30	0	10
B-35/65/0/10	35	0	10
B-40/60/0/10	40	0	10
B-50/50/0/10	50	0	10
B-10/87/3/10	10	3	10
B-15/82/3/10	15	3	10
B-20/77/3/10	20	3	10
B-25/72/3/10	25	3	10
B-30/67/3/10	30	3	10
B-35/62/3/10	35	3	10
B-40/57/3/10	40	3	10
B-50/47/3/10	50	3	10
B-10/85/5/10	10	5	10
B-15/80/5/10	15	5	10
B-20/75/5/10	20	5	10
B-25/70/5/10	25	5	10
B-30/65/5/10	30	5	10
B-35/60/5/10	35	5	10
B-40/55/5/10	40	5	10
B-50/45/5/10	50	5	10
B-30/67/3/5	30	3	5
B-30/67/3/8	30	3	8
B-30/67/3/10	30	3	10
B-30/67/3/12	30	3	12
B-30/67/3/15	30	3	15
B-30/67/3/18	30	3	18

The samples are designed using the abbreviation B-a/b/c/-d, where a indicates percentage of R-PET, b indicates percentage of HDPE, c indicates percentages of compatibilizer, and d indicates screw speed.

The extrudates were cooled by cooling bath and pelletized immediately (In Figure 5.1).

Figure 5.1 Pelletizing of R-PET/HDPE Blend and granules.

The dogbone samples were prepared by injection molding (Engel) at barrel temperature of 240-260-265-270 °C. In Figure 5.2 shows the dog bone samples of injection.

Figure 5.2 Test Samples

5.3 Material Characterization

5.3.1 Mechanical analysis

Mechanical tests were performed in an Instron testing machine. Injection-molded dog-bone specimens were tested at room temperatures following TS EN ISO standards for tensile properties and notched Charppy impact strength. The reported values for all properties are the average of three measurements. Tensile test were carried out at 23±2°C with a standard load cell of 1 kN at constant crosshead speed of 5mm/min as shown in Figure 5.3. Test samples with a gauge length and width of 10 mm and 4 mm, respectively.

Figure 5.3 Tensile test machine

Impact properties of HDPE and its blends were studied using a Devotrans testing machine (Figure 5.4). Impact strength measurement was performed at ambient temperature using 6J load according to notched charpy test standarts. The test specimens with 4 mm in thickness, and 10 mm in width were prepared by injection molding. The impact resistance wasreported as impact strength (J/m^2) that was the failure energy divided by the cross section area of the sample.

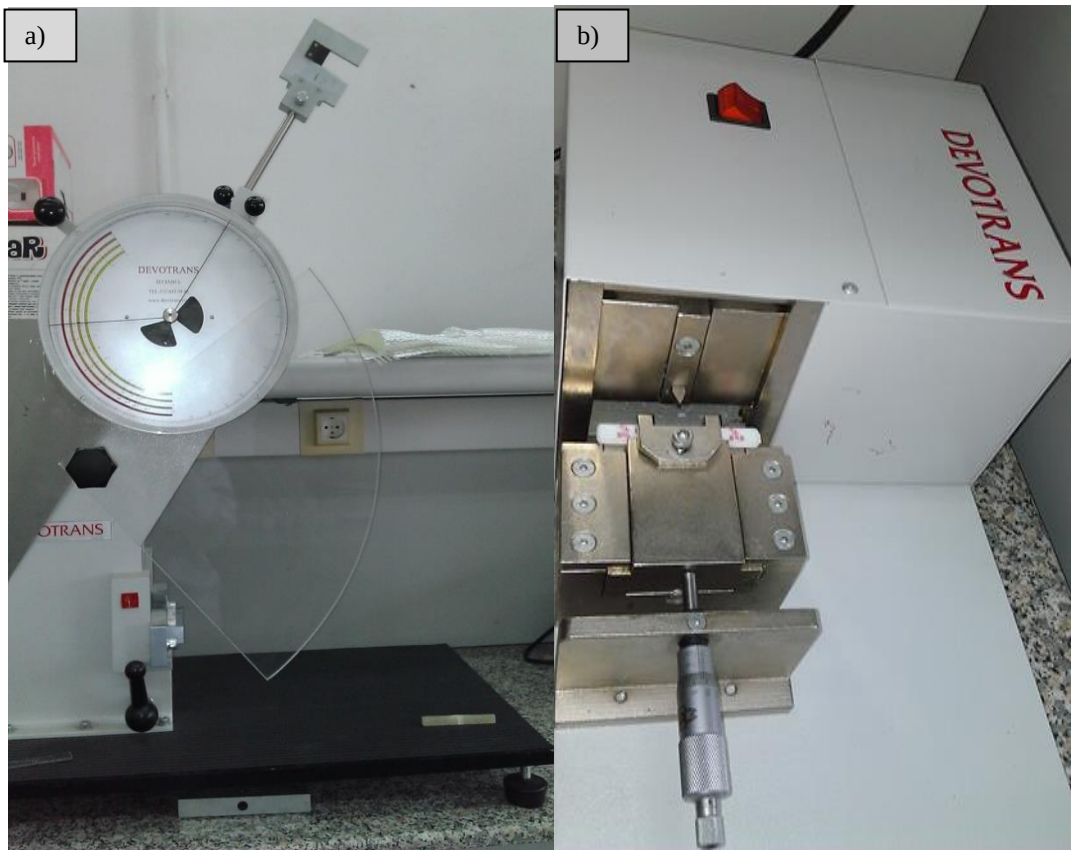

Figure 5.4: Impact test a) Charpy impact machine b) Notching machine

6. RESULT AND DISCUSSION

6.1 Blend Morphology

The two-phase morphology is occured, when two immisible polymers mix because of their chemical incompatibility**.** HDPE and R-PET are incompatible polymers which were used in this study. HDPE was major phase and it formed a matrix phase. On the other hand, R-PET dispersed in the form of droplet in the matrix phase which called a reinforcement phase. Figure 6.1 shows the SEM micrographs of R-PET/HDPE common reinforced blends. It can be seen that the common blend has a typical incompatible blend morphology which comprises dispersed phase (R-PET)and matrix phase(HDPE).

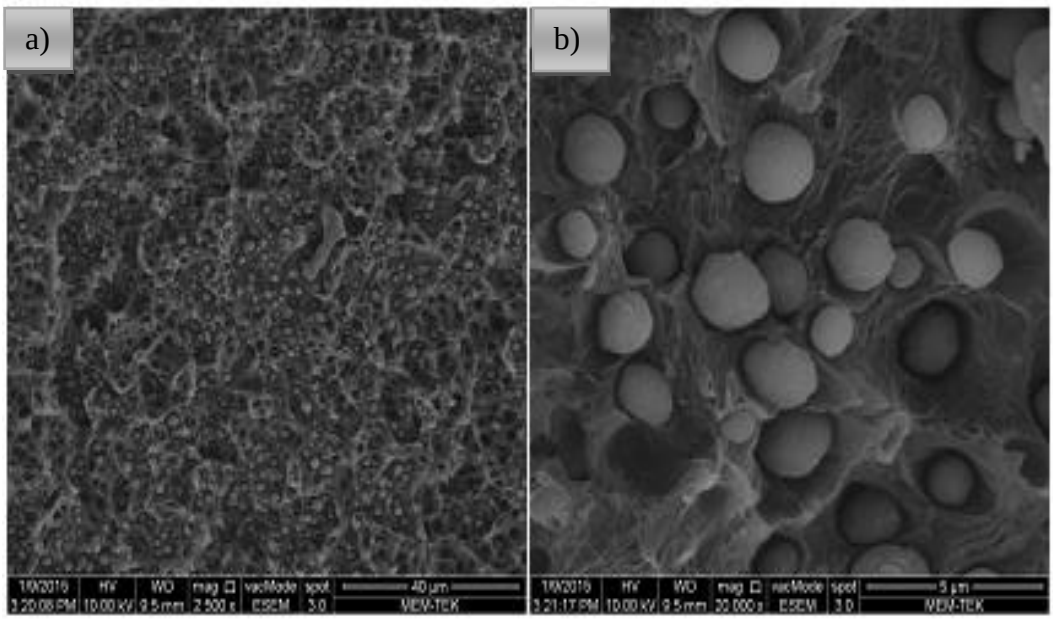

Figure 6.1 SEM micrographs of B-20/80/0/10 sample at different magnification a) 2500x magnification b)20000x magnification

In the same figure, the fractured surface of the blend strongly shows a gross phase separated morphology between the R-PET and the HDPE matrix. In addition, the presence of voids around the R-PET particles caused weak adhesion between R-PET and HDPE. These weak interphase adhesion caused the low tensile strength (Figure 6.10).

6.1.1 Effect of screw speed on the morphology

The influence of screw speed on the blend morphology was investigated by SEM analysis. R-PET/HDPE/E-EA-GMA (30/67/3) were extruded at different screw speeds (5,8,10,12,15 and 18 Hertz). The morphology phase evolution of R-PET/HDPE in the various samples is shown in Figure 6.2.

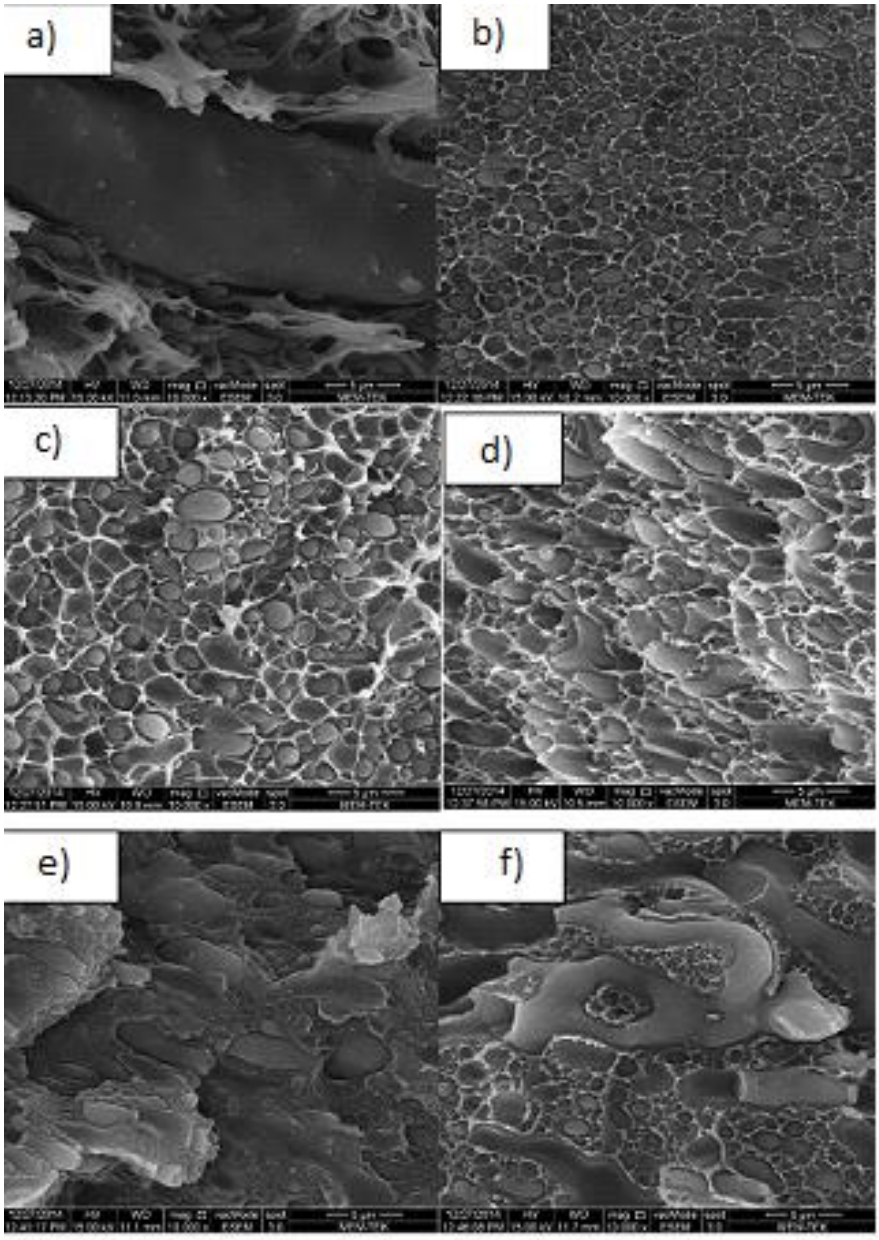

Figure 6.2 Effects of screw speed on the phase evolution of the blends. a)B-30/67/3/5, b)B-30/67/3/8, c)B-30/67/3/10, d)B-30/67/3/12, e)B-30/67/3/15, f)B-30/67/3/18 (x5000)

At the screw speed of 5 Hertz, PET is the dispersed phase in the PP matrix. However, the morphology is not homogeneous, because 5 Hertz is too slow to disperse R-PET drops. On the other hand at the screw speed of 8, 10, 12 hertz (Figure 6.2b,c,d), the

blend morphology is fine and screw speed causes intensive shear stress that facilitates efficient droplet breakup[35].

If the screw speed is between 15-18 Hertz , high shear rate induce a opposite effect and it cause to coalence of droplets. So the higher screw speed leads to phase inversion. Also this coarse morphology caused the weak mechanical properties.

6.1.2 Effect of concentration of R-PET on the morphology

The weight fraction of each polymers in the blend play an important role to determine the phase morphology. Minnor component forms dispersed phase and the major component forms the matrix phase. It is generally know that, the larger amount of component forms the matrix phase, while the smaller domains of polymer forms the dispersed phase. These situtation depends on several factors, such as viscoelastic properties of the polymers or the interfacial tension between the two phases[35]. When the weight ratios of the R-PET/HDPE blends are 10/90, 15/85, 20/80, 25/75, 30/70, 35/65, and 40/60, the dispersed phase is PET and the matrix is HDPE. SEM micrographs of fracture surfaces of R-PET/HDPE blends at different compositions are shown in Figure 6.3. The SEM observations provide that PET can be dispersed a spherical form in a HDPE matrix phase in all blends except B-50/50/0/10 (Figure 6.3d).

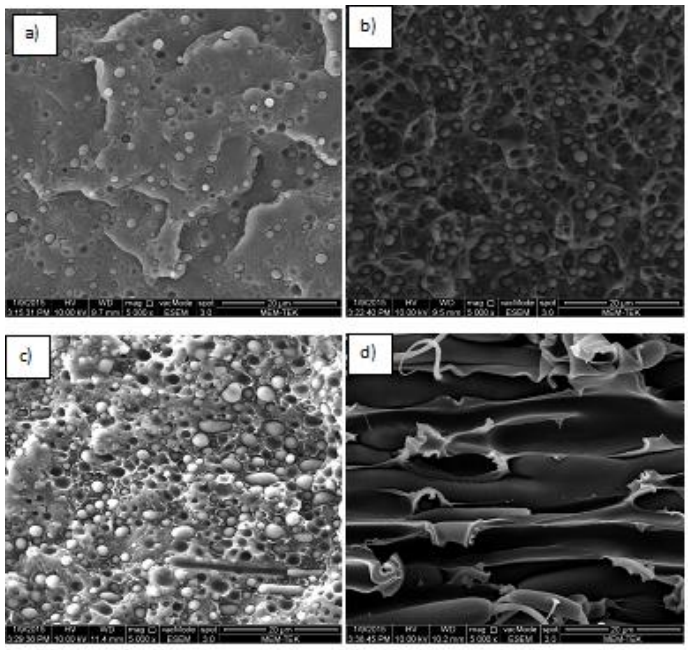

Figure 6.3 SEM micrographs of a)B-10/90/0/10, b) B-20/80/0/10, c)B-30/70/0/10, and d) B- 50/50/0/10 (x 5000)

The dispersed particle size increased with the concentration of R-PET (Figure 6.3). For example, when the concentration of R-PET was increased from 10wt% to 30, the particle mean diameter approximately increased from 1,60 μm to 3,18 μm. Further increase the concentration of R-PET to 50 wt%, the most spheres were deformed and gathered. The coalescence of drops induced the phase inversion morphology. The process of phase inversion can be followed in the images taken with SEM (Figure 6.3d).

6.1.3 Effect of compatibilizer and ratio on the morphology

R-PET and HDPE are immisible polymers and blending of these polymers caused the poor mechanical properties because of coarse morphology. In this study, to overcome these problems, third component was used which called compatibilizer. Compatibilizers generally consist of functionalized polymers such as block or graft copolymer.

E-EA-GMA compatibilizer is used in this study because it reacts with PET functional end groups. The addition of E-EA-GMA to R-PET/HDPE blends provided in remarkable changes in the morphology of blends. Figure 6.4 shows the SEM freeze-fractured surface of uncompatibilized (first column), 3 wt% compatibilized blends(second column) and wt%5 compatibilized blends. (10, 20,30 and 50 wt% R-PET and various concentration).

In the first column, the fractured surface of the samples apperantly indicates a coarse segregation morphology between the R-PET drops and the HDPE matrix. Also when the concentration of R-PET increases, the particle size of R-PET drops increase from 1,6μm to 3,18μm (As mention in chapter 6.1.1.).

The second and third column show SEM micrographs of the fractured surface of 3 wt% and 5 wt% E-EA-GMAin the R-PET/HDPE blends.The addition of E-EA-GMA in the blend induced a decrease of R-PET drops size. The decreased drop size provided a better adhesion polymer-polymer interface and homogenous morphology. The size reduction of dispersed phase in the matrix are clearly illustrated in Figure 6.5. According to Figure 6.4 and Figure 6.5, it can be conculuted that E-EA-GMA increased the interfacial adhesion between the R-PET and HDPE.

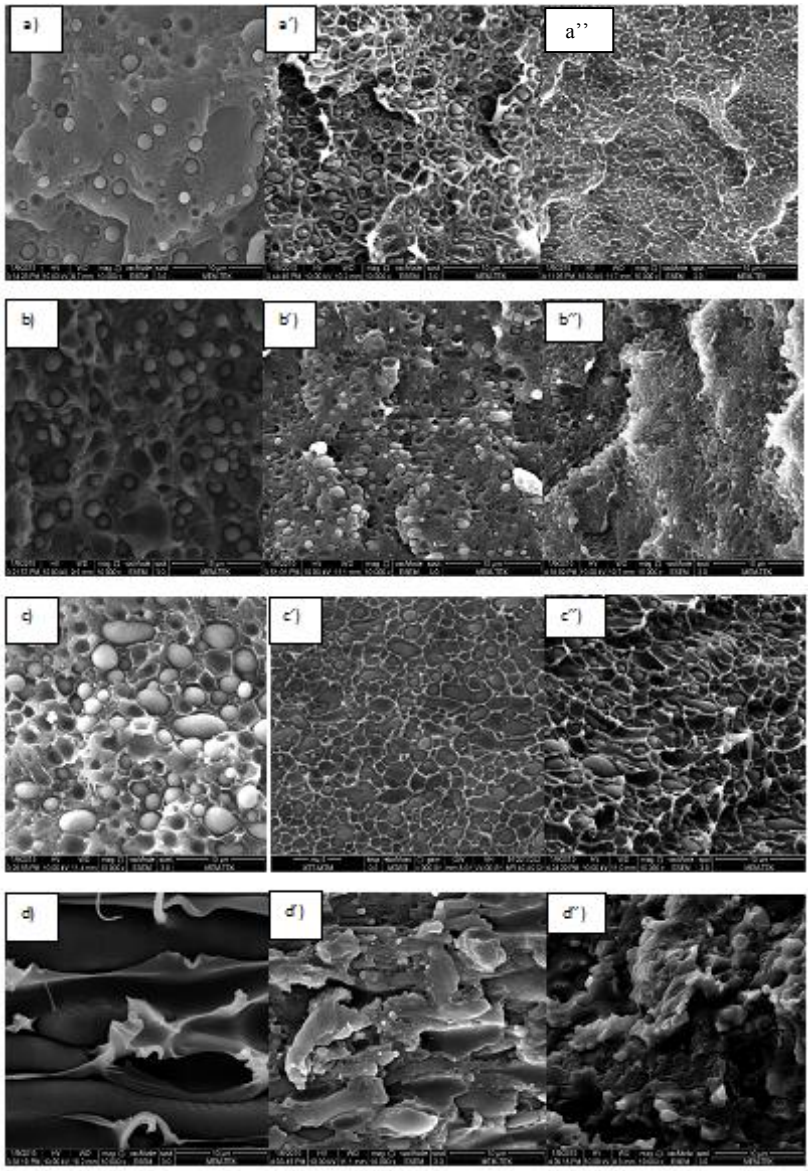

Figure 6.4 SEM micrographs a) B-10/90/0/10 b)B- 20/80/0/10 c)B- 30/70/0/10 d) B-50/50/0/10 ; a', b', c', d') %3 E-EA-GMA; a'', b'', c'', d'') %5 E-EA-GMA(x5000)

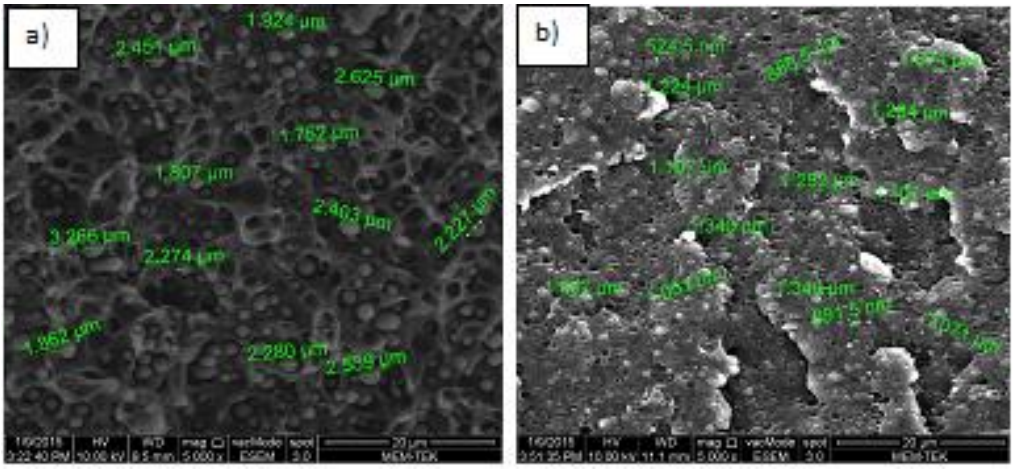

Figure 6.5 SEM micrographs of R-PET size reduction a)B-20/80/0/10, b) B- 20/77/3/10

Another effect of compatibilizer is that prevent to coalescence of PET droplets. As mention before, when the 50/50 R-PET/HDPE blends are prepared, the phase inversion can occur because of gathering of R-PET drops. When 3wt% and 5wt% E-EA-GMA was added in the 50/50 R-PET/HDPE blends, it is able to reduce the coalescence of R-PET droplets. As a result of addition compatibilizer, homogenous and droplets- matrix phase morphology was obtained (Figure 6.6).

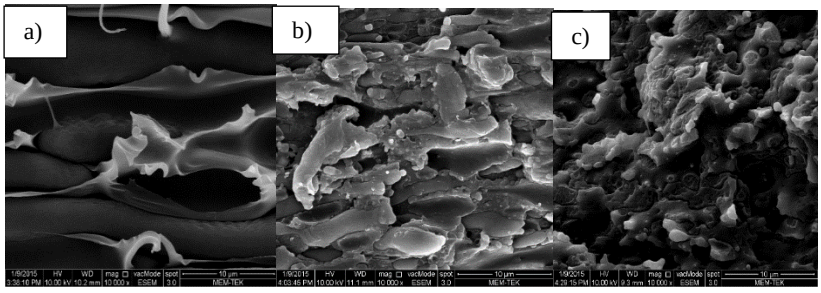

Figure 6.6 B-50/50/0/10 blends with different amounts of compatibilizer (E-EA-GMA) extruded at the screw speed of 10 hertz: (a) No compatibilizer (b) %3 E-EA-GMA c)%5E-EA-GMA

6.1.4 FTIR analysis

FTIR can be used to explain the mechanism of polymer miscibility in blends through hydrogen-bonding and through the changes in chemical structure. Figure 6.7 shows FTIR transmittance spectra for PET, EA-E-GMA, compatibilized and uncompatibilized blends. The C=O stretching of the ester group in E-EA-GMA and R-PET was seen by the appearance of absorption band at 1734 cm^{-1} and 1713 cm^{-1}, respectively. In the ternary blends, attention must be paid to the broadening of the PET carbonyl band at about 1725 cm^{-1}. This strong band belongs to the stretching vibration of the C= O groups. [36]

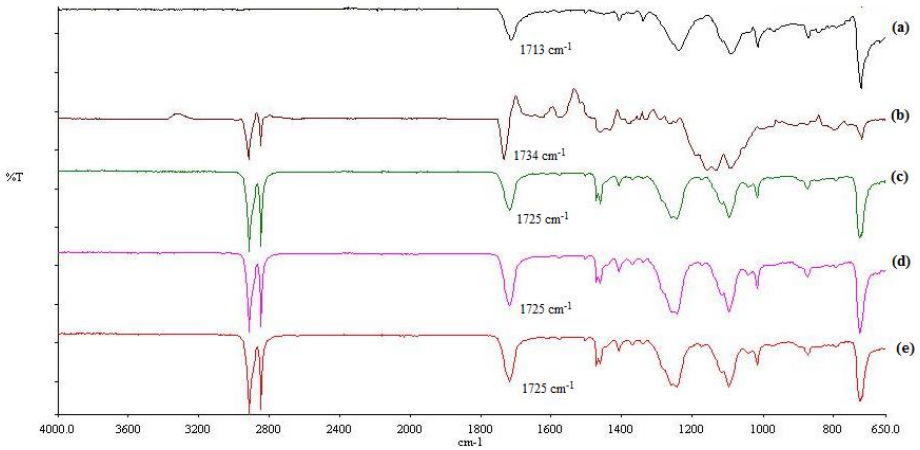

Figure 6.7 FTIR spectra of a) R-PET, b)E-EA-GMA c) B-30/70/0/10 (uncompatibilized), d)B-30/67/3/10 e)B-30/65/5710.

Figure 6.8 shows FTIR spectra of E-EA-GMA, HDPE, B-0/95/5/10, and B-50/45/5/10 at low wavelengths. The peak located at 912 cm^{-1} corresponding to the characteristic absorption band of GMA. It was disappeared in the base line of R-PET/HDPE/E-EA-GMA ternary blend. This can be explained with two reasons. The first reason is that the glycidyl epoxy groups of the compatibilizers (E-EA-GMA) reacted with the OH and COOH groups of PET.

The second reason is that the lower compotibilizer functional concentration caused to disappeared peak of GMA (912 cm^{-1}) in the R-PET/HDPE/E-EA-GMA blends. Because 5wt% E-EA-GMA is very small value when it compared with R-PET and HDPE concentration. It can be very smal impact on the FTIR peak. So B-0/95/5/10 blend was prepared to understand why of 912 cm^{-1} peak disappeared. According to FTIR results, the peaks of 912 cm^{-1} seemed for B-0/95/5/10 blends. But peak isn't sharp. Therefore the absence of absorption at 912 cm^{-1} in the R-PET/HDPE/E-EA-GMA blend can be provided the reactions between R-PET andE-EA-GMA .

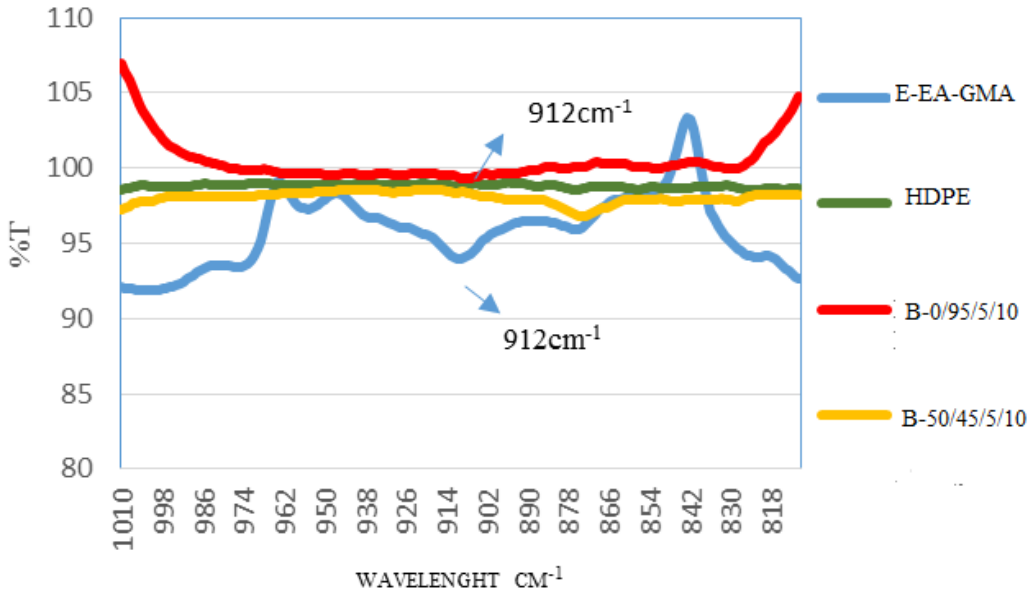

Figure 6.8 FTIR spectra a) E-EA-GMA ; b)HDPE; c) B-50/45/5/10 d) B-50/45/5/10.

6.2 Mechanical Properties of R-PET/HDPE Blends

6.2.1 Effect of screw speed

The effect of the rotation speed of screw on mechanical properties is presented in Figure 6.9 for the R-PET/HDPE blends with addition of 3wt%E-EA-GMA. Blends prepared at 8 and 10 Hertz screw speed showed the highest tensile strength.

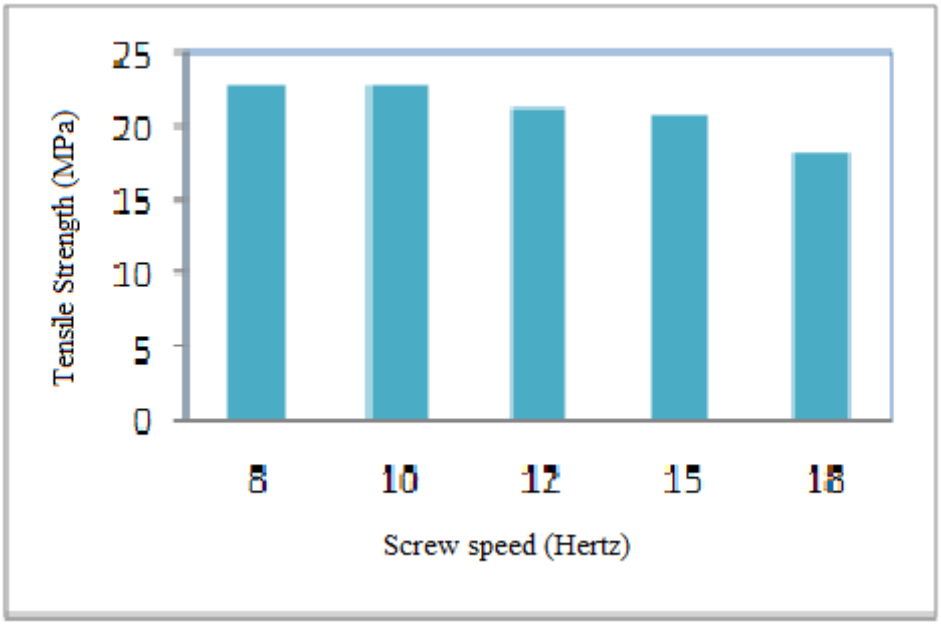

Figure 6.9 Mechanical properties of different screw rotation speed of R-PET/HDPE blends.

After 10 Hertz screw speed, tensile strength of the sample decreased. In other word, first two samples gave the best results. Since the extruder power is too high in the case of 8 Hertz, it was chosen as 10 Hertz, and after that the blends were prepared at this speed.

6.2.2 Effect of concentration R-PET.

Table 6.1 shows the tensile behavior of the R-PET/PE blends as a function of the R-PET amount. All curves display yielding in the same range of stress at yield 18-21 MPa. According to tensile test results, to increase the amount of R-PET didn't affect tensile stress even R-PET decreased the tensile strength. Also the tensile strenght of pure HDPE showed better results than the developed blends except % (35/65) R-PET/HDPE blend. It may be the coarse morphology and the lack of adhesion between HDPE and the R-PET. SEM images supported these results explained in the chapter 6.1.1. It was observed different sizes of the R-PET in the matrix HDPE, leading to a heterogeneous product and low mechanical properties.

The elongation at break of B-10/90/0/10 and B-50/50/0/10 are compared. It is observed that increasing of R-PET components causes the break in elongation to decrease to very low values. Elongation at break for 10% R-PET added blend is very high and the lenght of tensile machine wasn't enough to break the dog-bone samples of HDPE rich blend. On the other hand, elongation at break decreased dramatically

with increasing R-PET amount in the blend and it has the minimum value for 50/50R-PET/PE blends (%2 elongation at break) (Figure 6.10).

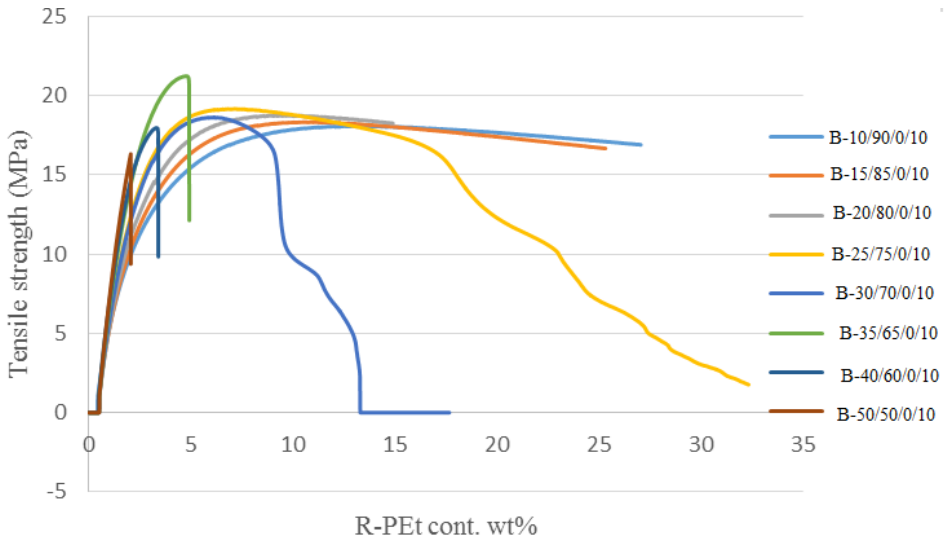

Figure 6.10 Tensile strength of different R-PET amounts of polymer blends

On the other hand, Young modulus values depend strongly on R-PET concentration. (Table 6.1)

Table 6.1: Mechanical properties of HDPE, R-PET, uncompatibilized HDPE/R-PET blends

Sample	Tensile strenght (MPa)	Young's modulus (GPa)	Izod impact strenght (J/m^2)
HDPE	20	0,95	43
R-PET/HDPE (10/90/0-10)	19	0,8	19,5
R-PET/HDPE (15/85/0-10)	18	0,9	16,2
R-PET/HDPE (20/80/0-10)	19	1	8,2
R-PET/HDPE (25/75/0-10)	19	1	7,2
R-PET/HDPE (30/70/0-10)	19	1,1	6,5
R-PET/HDPE (35/65/0-10)	21	1,2	5,6
R-PET/HDPE (40/60/0-10)	18	1,3	5,4
R-PET/HDPE (50/50/0-10)	18	1,4	5,33

Young's modulus increased with increasing R-PET concentration. For example, the tensile modulus enhances from 0,95GPa to 1,4GPa with 50 wt% R-PET addition. These results are supported by the study of Avila *et. al.* They used three different PET amount in the PET/PE blends and Young modulus increased with addition of PET[37]. The optimum R-PET amounts are 20wt% or more for increment of modulus. This is an expected result, since PET is stiffer than HDPE.

6.2.3 Effect of compatibilizer content

The effect of compatibilization on the mechanical properties was tested when different ratios of compatibilizer were added for R-PET/PE blends.Table 6.2 shows the tensile behavior of the R-PET/PE blends as a function of the R-PET amount ranging from 0 to 50 wt% and the compatibilizer ratio The mechanical properties of the blends are related to the phase morphology. As mention before, morphology of an immiscible polymer blend induces low mechanical properties compared to the pure components. As expected, the addition of different ratio compatibilizers caused an improvement in tensile strength, elongation at break and impact strength of the R-PET/HDPE blends as shown in Table 6.2. Figure 6.11 shows the tensile strength of R-PET/HDPE and R-PET/HDPE/ E-EA-GMA blends plotted as a function of the weight ratio of R-PET and compatibilizer ratio.

In the case of E-EA-GMA compatibilized blends, the tensile strength values of compatibilized blends are higher than all the uncompatibilized blends. This is an evidence of improved adhesion in the two phases of compatibilized blends. As shown in Table 6.2, the overall improvement of the mechanical properties after compatibilization is very obvious. For tensile strength and elongation at break have been increased dramatically. The optimum amount of the E-EA-GMA compatibilizer for the R-PET/HDPE is 3wt%. Because higher content of the compatibilizer didn't give rise to further significant improvement in the mechanical properties. The highest or equal (tensile strength of %5wt compatibilized blend) tensile strength were obtained in all 3wt% compatibilized blends.

In the case of 3wt% E-EA-GMA compatibilized blends, tensile strength increase from 18 MPa to 26 MPa and tensile strain at break increase from 2 to about 4,5%. In addition 5wt% E-EA-GMA compatibilized blends, tensile strength increase from 18 MPa to 25 MPa and tensile strain at break increase from 2 to about 4,5%.

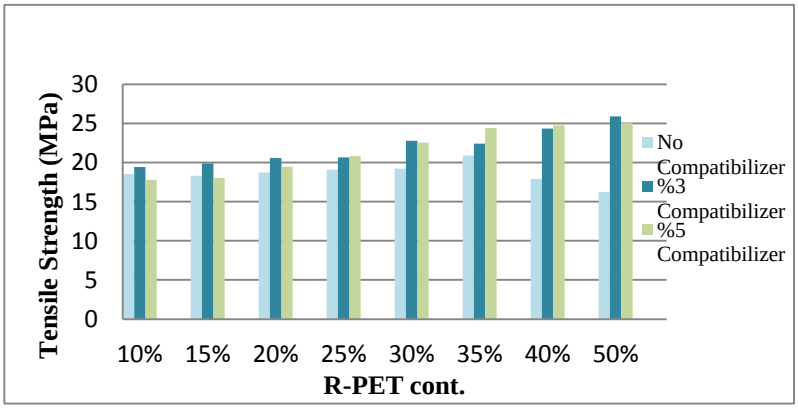

Figure 6.11 The effect of compatibilizer and contents on the tensile strength of HDPE/PET blends

As seen from Table 6.2, the blend with 5wt% E-EA-GMA had similar tensile properties and elongation at break to the sample with 3wt%.Contrary to tensile strength, the modulus was adversely affected by the compatibilizer amount due to elastomeric behavior of these copolymers. The Young's modulus of the compatibilized blends is lower than that of the uncompatibilized blends (Figure 6.12)

Table 6.2: Mechanical properties of HDPE, R-PET, compatibilized HDPE/R-PET blends

Sample code	Tensile Strenght (MPa)	Young's Modulus (GPa)	Izod İmpact strenght (J/m2)
R-PET/HDPE (10/90/3/10)	19,44	0,86	21,5
R-PET/HDPE (15/85/3/10)	19,86	0,979	9,3
R-PET/HDPE (20/80/3/10)	20,56	0,97	9,7
R-PET/HDPE (25/75/3/10)	20,66	1,01	8,2
R-PET/HDPE (30/70/3)	22,8	1,09	8,2
R-PET/HDPE (35/65/3/10)	22,41	1,075	7,4
R-PET/HDPE (40/60/3/10)	24,36	1,15	6,8
R-PET/HDPE (50/50/3/10)	26	1,23	6,2
R-PET/HDPE (10/90/5/10)	17,8	0,82	11,2
R-PET/HDPE (15/85/5/10)	18,04	0,84	9,9
R-PET/HDPE (20/80/5710)	19,47	0,936	9,9
R-PET/HDPE (25/75/5/10)	20,8	0,99	8,10
R-PET/HDPE (30/70/5/10)	22,55	0,98	7,4
R-PET/HDPE (35/65/5/10)	24,42	1,07	6,8
R-PET/HDPE (40/60/5/10)	24,74	1,132	5,2
R-PET/HDPE (50/50/5/10)	25,04	1,2	4,6

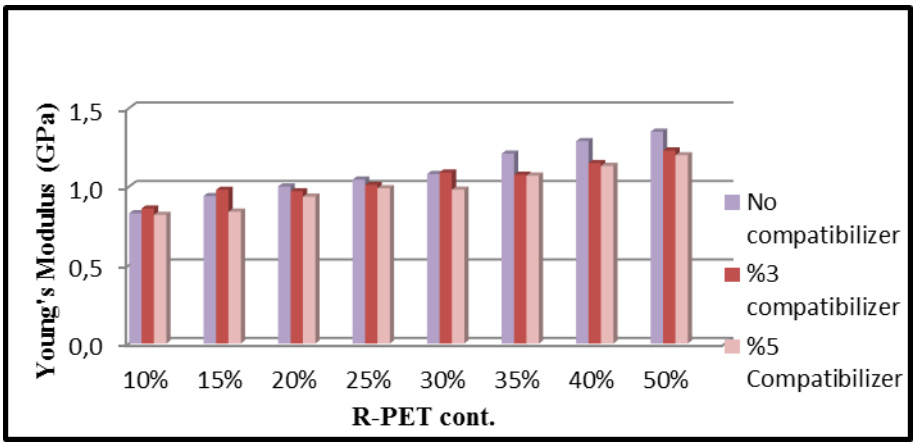

Figure 6.12 The effect of compatibilizer contents on the elastic modulus of R-PET/ HDPE

In this study, HDPE was used for impact modifier of PET. But for the binary blends, sharp decrease of the impact strength is observed when the R-PET content increases from 10 to 50wt% (Table 6.2). After 10wt% R-PET addition, the impact strength decreased to the double of original value because of R-PET britttle behaviour. The addition of 3wt% and 5% of E-EA-GMA slightly improves the impact strength of the blends (Table 6.2).

7. CONCLUSIONS

The objective of this thesis was to develop new blend materials based on R-PET and HDPE polymers. This was achieved by blending HDPE as a matrix, and R-PET reinforced polymer and E-EA-GMA as a compatibilizer.

R-PET/HDPE blends were examined by SEM FTIR and Universal Testing Machine.

In this context, R-PET/HDPE blends were prepared at different screw speeds in order to achieve homogenenous drops morphology. 10 Hertz of screw speed was chosen among them due to its dispersibility and processability.

During these studies, a decrease in the tensile properties of blend (30wt% R-PET) was observed after increasing the screw speed above 10 Hertz of screw speed. Because R-PET droplets didn't have enough time to disperse homogenously at higher screw speeds.

During these studies, it was observed that the morphology of droplets also depent on R-PET concentration. According to the morphological images, dispersed particle sizes increaced simultanously by increasing R-PET concentration. When R-PET concentration reached to %50wt, droplets coalesced and the phase inversion occurred.

R-PET and HDPE are known as immissible polymers therefore compatibilizers are used to decrease interfacial tension and achieve homogeneous morphology. During our study, E-EA-GMA was used ~~for~~ as a compatibilizer because it can react with both OH and COOH groups of R-PET and also increase the interface adhesion between the polymers.

According to the results, there was a significant improvement of mechanical properties of compatibilized blends compared to the uncompatibilized ones. Tensile strength was improved dramatically while 3wt% compatibilizer was added to the blend. Adding more compatibilizer to the blends didn't give remarkable results than 3wt%. Therefore, it is well understood that 3wt% is an optimum value for this study. On the other hand, the mechanical properties of the compatibilized R-PET/HDPE blends showed an important improvement compared to the neat HDPE. For example,

Young's modulus of neat polymer increased almost %47 of R-PET due to its reinforcement effect. In these cases, the increase of Young's modulus was about 47% but the decreasing of elongation at break and impact strength were very sharp.

Overall of these results, determinated R-PET/ HDPE blends will be used to produce plastic pipes in an ongoing project (SANTEZ).

REFERENCES

[1] Polymer blends. http://shodh.inflibnet.ac.in/. [Online] 1985. [Cited: september friday,2014.] http://shodh.inflibnet.ac.in:8080/jspui/bitstream/123456789/572/3/03_chapters.pdf.

[2] **Barlow, D. R. Paul and J. W.** A (1979) Brief Review of Polymer Blend Technology. Austin American Chemical Society, 17, 315-335

[3] Utracki, L. A. (2000) Polymer Blends Handbook . London : *Kluwer Academic Publishers*, 1-4020-1110-5.

[4] Prochazka F., Carrot C., Castro M., Celle C. and Majesté J-C. Phase Inversion and Cocontinuity in Immiscible Polymer Blends, France

[5] Kim, D. H., Park K. Y., Kim, J.-Y., Kim K. D. S., (2000), Improved Compatibility of High-Density Polyethylene/Poly(ethylene terephthalate) Blend by the Use of Blocked Isocyanate Group. *John Wiley & Sons, Inc*, 1017-1024

[6] **Robeson, Lloyd M.** Polymer Blends a Comprehensive Review. s.l. Hanser. 10: 3-446-22569-2

[7] Polymer blends . Polymer and Material Chemistry. [Online] june 2, 2010. [Cited:october 8, 2014.] http://www.polymat.lth.se/courses/mat_func/mat_ func_pdf/ Patrics%20 hand-out%203.pdf.

[8] Composites.. [Online] . [Cited:october 16, 2014.]http://shodhganga.inflibnet. ac. in/bitstream/10603/15830/12/12_chapter%201.pdf

[9] Puyvelde, P. V., Velankar, S., Moldenaers P. (2001)Rheology and Morpho logy of Compatibilized Polymer Blends. Current Opinion in Colloid & Interface Science., 457-463.

[10] Utracki, L.A., (1989), Polymer Alloys and Blends: Thermodynamics and Rheology., The Canadian Journal of Chemical Engineering,volume80

[11] Yoon, P.J. and White, (1994) J.L.J. *Appl. Polym. Sci.*, Vol. 51, 1515.

[12] White J.L. and Bumm S.H., (2011) Polymer Blend Compounding and Processing. *Encyclopedia of Polymer Blends:* Volume 2: Processing,.1-23

[13] Particlesciences.[Online][Cited: agust 17, 2013.].www.particlesciences.com/news/technical-briefs/2011/hot-melt-extrusion.html.

[14] Khonakdar, H.A., Jafari, S.H., Mirzadeh,S., Kalaee, M.R., Zare, D., 1 Saeb, M.R., (2013) Rheology-Morphology Correlation in PET/PP Blends: Influence of Type of Compatibilizer. Iran : *Wiley Online Library,* 10.1002/vnl.20318.

[15] Imamura, N., Nishimura, H., Sakamoto H. and Kawasaki S.,(2011) Evaluation Of Mechanical Properties Of Used Materials For Plastic Recycle. s.l. :ANTEC, Vols. 3-8.

[16] Johari, A. P., Jain, D., Singh, R. K., Development of Polyester PE Post Consumer Scrap Alloy, İndia.

[17] Puyvelde, P. V., Moldenaers P. (2005), Rheology and Morphology Development InImmıscıble Polymer Blends, Belgium : *The British Society of Rheology*. 101 - 145

[18] Wenjing, L., (2009) PET/PP-Based Polymer Composites: Effects of Compatibilizer and Nanofillers on the Processing- Structure-Property Relationships" M.Sc.

[19] Fortelný, I., (2006), Phase Structure Formation And Evolution İn Polymer Blends, CSc

[20] Yao, L., and Beatty C., (1994), The in situ Compatibilization of HDPE/PET Blends, *Imaging and Image Analysis Applications*, 89-95

[21] Jabarin, S. A., Lofgren, E. A., and Shah, S. B., (1992) High-Density Polyethylene/Poly(ethyleneterephthalate) Blends, *American Chemical Society*, 215-235

[22] Pracella, M., Pazzagli, F. and Gales, A. (2002), Reactive Compatibilization and Properties of Recycled Poly(ethylene terephthalate)/Polyethylene Blends. *Polymer Bulletin.*

[23] Kalfoglou, N. K., Kafidas D. S., Kallitsis J. K., (1995) Comparison of compatibilizer effectiveness for HDPE-PET , Polymer, 4453-4462.

[24] Pluta, M., Bartczak, Z., Pawlak, A., Galeskı, A., Pracella M., Mırosław P. (2001), Phase structure and viscoelastic properties Of Compatibilized blends Of PET and HDPE Recyclates, Journal of Applied Polymer Science. Vol. 82, 1423–1436.

[25] Pracella, M., Rolla, L., Chionna, D., Galesk, A., (2003), Compatibilization and Properties of Poly(ethylene terephthalate) /Polyethylene Blends Based on Recycled Materials. Macromol. Chem. Phys. 1473–1485

[26] Pracella, M., Pazzagli, F., Galeski, A., (2002) Reactive compatibilization and properties of recycled poly(ethyleneterephthalate) /polyethylene blends" Polymer B ulletin 48, 67-74

[27] Pawlak, A., Morawiec, J., Pazzagli, F., Pracella M., Galeski A.,(2002), Recycling of Postconsumer Poly(ethylene terephthalate) and High-Density Polyethylene by Compatibilized Blending, *Journal of Applied Polymer Science*, 1473-1484.

[28] Fasce, L., Seltzer, R. and Frontini, P., (2005) Mechanical and Fracture Characterization of 50:50 HDPE/PET Blends Presenting Different Phase Morphologies . Polymer Engıneerıng And Scıence, 354-363

[29] Chareunkvun, S., (2007) A Study of Compatıbılızatıon and Properties of Recycled Hıgh Densıty Polyethylene (HDPE)/Polyethylene Terephthalate blends, Suranaree University of Technology.

[30] J.K. **Lee, C.D. Han** , (2000) Polymer 41 1799–1815

[31] Guerrero, Carlos, et al., (2001) Properties And Morphology Of Poly(Ethylene Terephthalate) and High-Density Polyethylene Blends. *Journal of Applied Polymer Science*, Vol. 82, 1382–1390.

[32] Lei Y., Wu, Q., Clemons, C. M., Guo W., (2009)Phase Structure and Properties of Poly(ethylene terephthalate)/High-Density Polyethylene Based on Recycled Materials. Journal ofAppliedPolymer Science. Vol. 113, 1710–1719.

[33] Jarukumjorn K. and Chareunkvun S. (2006), Compatıbılızatıon of Recycled Hıgh densıty Polyethylene (HDPE)/polyethyleneTerephthalate (PET) Blends, Suranaree J. Sci. Technol. 14(1):1-8

[34] Jabarin, S.A and Bhakkad, V.V., (1995), Morphology and Properties of Poly(ethylene terephthalate)-High Density Polyethylene Blends : Effects of Processing Variables. Plastics, Rubber, and Paper Recycling.

[35] Li W., Schlarb, A. K., Evstatiev M., (2009), Influence of Processing Window and Weight Ratio on the Morphology of the Extruded and Drawn PET/PP Blends" *Society of Plastics Engineers.*

[36] Brandalise R. N., Mauler R. S., Zeni M., (1996) Blends Of Hıgh Densıty Polyethylene And Poly(Ethylene Terephthalate)

[37] Villa, F. A., Duarteb M. V., (2003), Polymer Degradation and Stability 80 373–382

CURRICULUM VITAE

Name Surname: Tuğba Güven

Place and Date of Birth: 09.04.1988

E-Mail: **tugbagvn@gmail.com**

EDUCATIONAL INFORMATION

University: Yildiz Technical University(Chemistry-Metallurgy/ Chemical Engineering) **CGPA:** 2.90 / 4.00

High School: Çanakkale Fen Lisesi **CGPA: 4.90 / 5.00**

WORK EXPERIENCE INFORMATION

19.11.2012- Mir Arge / Chemical Engineer

06.2010-07.2010 Kalekim Aş. Intern Engineer

07.2009-08.2009 Etibor Maden İşletmeleri Intern Engineer

PROJECTS

SAN-TEZ Project

Teydep Project

Design of a Waste Disposal Facility

Acrylic Acid Plant Design

Characterization of clay mineral of the Experimental Design