TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

LOTTA MANTERE

FUNCTIONAL POLYETHYLENE AS A COMPATIBILIZER IN BLENDS OF RECYCLED POLYETHYLENES AND POLYAMIDES

Master of Science thesis

Examiner: prof. Jurkka Kuusipalo
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ABSTRACT

LOTTA MANTERE: Functional Polyethylene as a Compatibilizer in Blends of Recycled Polyethylenes and Polyamides
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The recycling of polymeric materials consisting of multiple different polymer types is complex as most of the common thermoplastics are immiscible with each other. The reactive compatibilization of immiscible polymer blends with functionalized reactive polymers is a well-known method and in this thesis the same method is utilized in blending of recycled polymer material with virgin polyethylene. The objective of this thesis is to evaluate how a commercial polyethylene behaves as a matrix material for polyamides when a maleic anhydride grafted polyethylene, is used as a compatibilizer precursor, CP in the blend and how the behaviour changes if neat polyamide is replaced as the dispersed phase with recycled packaging film waste, known to contain at least polyethylene and polyamide.

A set of compounds was prepared by reactive compounding. In the compounds polyethylene was used as a matrix material with and without added PE-g-MA CP in it. The minor phase in the compounds was either polyamide or a blend of recycled material known to contain at least polyethylene and polyamide. The blend composition was varied by altering the content of CP and the minor phase. The effects of the compound compositions on the behaviour of the matrix material and the compatibilization efficiency was evaluated by characterisation of the mechanical, morphological, thermal and melt flow properties.

The result show that the studied CP showed strong compatibilization efficiency towards the virgin blends of PE and PA. The addition of CP increased the impact strength and elongation at break for 85/15 PE/PA blends. Also the particle size of the dispersed PA phase decreased as the CP decreased the interfacial tension between the phases. It is clear by the results that the addition of CP in the PE matrix increases the adhesion between the PE and PA phases. The blends containing recycled material as the dispersed phase showed slightly poorer mechanical properties but the morphology of the 70/30 PE/recycled blend was even finer than that of compatibilized 85/15 PE/PA blend, no matter if the recycled blend was compatibilized or not.

TIIVISTELMÄ

LOTTA MANTERE: Funktionaalisen polyeteenin käyttö kompatibilisaattorin esiasteena kierrätettyjen polyeteenien sekä polyamidien seoksissa.
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Useasta eri polymeerityypistä koostuvan muovijätteen kierrätys on haasteellista, koska suurin osa käytetyimmistä kestomuoveista ovat sekoittumattomia keskenään. Sekoittumattomien polymeeriseosten reaktiivinen kompatibilisointi funktionalisoiduilla polymeereillä on tunnettu menetelmä ja tässä työssä samaa menetelmää käytetään kierrätetyn polymeerijätteen seoksissa neitseellisen polyeteenin kanssa. Työn tavoitteena on arvioida kaupallisen polyeteenin käyttäytymistä matriisimateriaalina polyamidille, kun maleiinihapon anhydridilla oksastettua polyeteeniä käytetään seoksessa kompatibilisaattorin esiasteena, CP. Tavoite on myös tutkia, miten polyamidin korvaaminen kierrätetyllä pakkausjätteellä jonka tiedetään sisältävän ainakin polyeteeniä sekä polyamidia vaikuttaa matriisin käyttäytymiseen.

Työssä valmistettiin joukko polymeeriseoksia reaktiivisella kompaundoinnilla. Seoksissa käytettiin matriisimateriaalina polyeteeniä PE-g-MA CP:lla sekä ilman. Seoksen dispergoituneena faasina käytettiin joko polyamidia tai kierrätettyjen materiaalien seosta, jonka tiedettiin sisältävän ainakin polyeteeniä sekä polyamidia. Seoksen koostumusta vaihdeltiin muuttamalla CP:n sekä dispergoituneen faasin osuutta. Seoksen koostumuksen vaikutusta matriisin toimintaan sekä kompatibilisointikykyyn arvioitiin karakterisoimalla mekaanisia, morfologisia, termisiä sekä sulavirtausominaisuuksia.

Tulokset osoittivat käytetyn kompatibilisaattorin kompatibilisoivan tehokkaasti neitseellisiä polyeteenin ja polyamidin seoksia. Lisäämällä CP:ta seosten iskulujuus sekä murtovenymä kasvoivat huomattavasti 85/15 PE/PA seoksissa. Myös dispergoituneen polyamidin partikkelikoko pieneni huomattavasti CPn pitoisuuden kasvaessa seoksessa. Tulokset osoittivat myös, että CP:n lisääminen seokseen lisäsi faasien välistä adheesiota. Kierrätettyä materiaalia sisältävillä seoksilla oli hieman heikommat mekaanisia ominaisuuksia, kuin neitseellisillä seoksilla, mutta morfologialtaan 70/30 PE/kierrätetty materiaali seos oli jopa hienompijakoisempi kuin neitseellinen, kompatibilisoitu 85/15 PE/PA seos, riippumatta siitä, sisälsikö kierrätetty seos CP:ta vai ei.

PREFACE

This Master’s Thesis has been done for Borealis Polymers and within ARVI – Material value chains project by CLEEN, Cluster of Energy and Environment. The funding for the thesis was provided by the Industrial Research Fund of Tampere University of Technology and the materials, equipment and laboratory facilities for conducting the tests were provided by Borealis Polymers. I would like thank both of these parties for making my thesis project possible.

I wish to thank my academic supervisor and examiner professor Jurkka Kuusipalo for guiding, providing the contacts to Borealis and for the subject of the thesis. I would also like to thank my industrial supervisor Andrei Ollikainen from Borealis Polymers for the patience and all the advice during the process. I am grateful for the advice and new point of views given by the support group from Borealis, that is, Auli Nummila-Pakarinen, Mikko Peltovuori, Juha Hartikainen and Kshama Motha. Big thanks go also to the other co-workers at Borealis Polymers for helping me with the tests and other related matters, such as giving me some distraction from the thesis during the coffee breaks.

Seven years has passed since I first stepped the TUT campus as a freshman. Besides the degrees of B.Sc. and M.Sc. in Technology I have gained lots of new experiences, memories, contacts and, most of all, friends, hopefully for life. Special thanks go to a certain sporrrts team that has supported me with their original way through my years at TUT.

Most of all, I wish to thank my family for the support and believing in me through this thesis project and also through the whole 7 year period that it took for me to finish my studies. Especially I thank my sister Laura for answering the phone always when I needed. I could not have made it without you!

Kilpilahti, Porvoo 29.06.2015

Lotta Mantere

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LIST OF SYMBOLS AND ABBREVIATIONS

CLEEN	Cluster of Energy and Environment
CB	complete break in the Charpy impact test
CP	compatibilizer precursor
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
EAA	ethylene acrylic acid
EBA	ethylene butyl acrulate
EGMA	ethylene glycidyl metchacrylate copolymer
EMAA	polyethylene methacrylic acid
EPDM	ethylene propylene diene rubber
EU	European Union
EVA	ethylene vinyl acetate
FTIR	Fourier transform infrared
GMA	glycidyl methacrylate
GMP	Good Manufacturing Practice
HB	hinge break in the Charpy impact test
HDPE	high density polyethylene
IR	infrared
ISO	International Organization for Standardization
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MA	maleic anhydride
MAH	see MA
MFR	melt flow rate
MW	molecular weight
MWD	molecular weight distribution
NB	no break in the Charpy impact test
PA	polyamide
PB	partial break in the Charpy impact test
PE	polyethylene, bimodal Borstar® polyethylene in the experimental part
PET	polyethylene terephthalate
PMMA	polymethyl methacrylate
PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
REACH	EU regulation for the Registration, Evaluation, Authorization and Restriction of Chemicals
rHDPE	recycled HDPE
SAXS	small-angle X-ray scattering
SEBS	ethylene butylene styrene copolymer
SEM	scanning electron microscope
SEP	styrene ethylene propylene copolymer
SPI	Society of Plastic Industry
TEM	transmission electron microscope
TGA	thermogravimetric analysis
WAXS	wide-angle X-ray scattering

δ	solubility parameter
ε_B	elongation at break
ε_Y	elongation at yield
η	melt viscosity
ρ	density
σ_B	stress at yield
σ_M	maximum tensile stress
σ_Y	stress at yield
ϕ_i	volume fraction of the phase *i* in polymer blend
χ	Flory-Huggins interaction parameter
ΔC_p	heat capacity increment at the glass transition
E_t	tensile modulus
ΔH	Enthalpy of phase transition
R	ideal gas constant
T	temperature
Tc	crystallization temperature
Tm	melting temperature
v	molar volume

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1. INTRODUCTION

The demand for plastics increases every year and the biggest application area for plastics is packaging which covers, for example, over one third of the plastic demand in the European Union, EU. The environmental awareness of the consumers and the new regulatory in the waste disposal have increased the demand for new approaches in plastic waste management. For example many countries have set a landfill ban for plastic waste and therefore new options for the waste management are needed. [1; 2]

The waste hierarchy of the EU prefers mechanical recycling over the recovery as energy. This, however, can be sometimes rather difficult because many plastic applications and especially packaging materials contain more than just one type of plastic, for example the multilayer packaging films comprise often at least of three different layers, two different thermoplastics and a tie layer between them. As most of the most used thermoplastics are immiscible with each other due to the large dimensions of the macromolecules and differences in the polarity, the mechanical recycling may result in blends with minimal adhesion between the blend phases and, hence, the mechanical properties of the end products are weak. [1; 3]

The miscibility of polymers depends on the thermodynamics of the mixed system and it is affected by size, structure and polarity of the mixed components. When two polymers are immiscible with each other two separate phases are formed. This phase separation can be controlled by compatibilization. The addition of a compatibilizer promotes interactions between the blend components and thereby the immiscible blend results in macroscopically uniform physical properties throughout its whole volume. The compatibilizers are usually block or graft copolymers that locate to the interface of the blend components by interpenetrating from one phase to another with blocks miscible with each component. Compatibilization of immiscible polymer blends is a well-known method for creating new property combinations for polymeric materials. Now, it has been suggested to be one solution for solving the challenge of immiscibility of plastic waste in mechanical recycling. [4-6]

A common pair of thermoplastics used in food packaging films is a combination of polyethylene, PE and polyamide, PA. Polyethylene offers sealability, processability, flexibility, impact strength and moisture insensitivity, whereas polyamide offers strength, thermal stability and barrier properties against oxygen and aroma. The immiscible blends of polyethylene and polyamide have been studied extensively over the years, and many suitable compatibilizers and compatibilizing methods have been found. An example of these methods is to use functionalized polyethylene as a compatibilizer precursor, CP in the PE/PA blends. The functionalities on PE backbone, such as maleic anhydride, MA may then during reactive extrusion react with the amine end groups of polyamide and thereby form a graft copolymer, PE-g-PA which can act as a compatibilizer at the phase interface. [4; 7-34]

The objective of this thesis is to evaluate how a commercial Borstar® polyethylene behaves as a matrix material for polyamides with different viscosity when a maleic anhydride grafted polyethylene, PE-g-MA, is used as a compatibilizer precursor in the blend. The intent is also to study changes in the matrix behaviour as the neat polyamide is replaced with packaging film waste, known to contain at least polyethylene and polyamide.

In this thesis a set of compounds was prepared by reactive extrusion using a co-rotating twin-screw extruder. In the compounds a Borstar® polyethylene was used as a matrix material with and without added PE-g-MA CP in it. The minor phase in the compounds was either polyamide with low or medium viscosity or a blend of recycled material made of packaging films known to contain at least polyethylene and polyamide. The blend composition was varied by altering the content of CP and the minor phase. The effects of the compound compositions on the behaviour of the matrix material and the compatibilization efficiency was evaluated by characterisation of the mechanical, morphological, thermal and melt flow properties. The compounds with different matrices and minor phases were compared to each other and it was assessed how the use of recycled blend differs from the use of virgin polyamide as the dispersed minor phase.

The thesis is a part of ARVI - Material Value Chains research organized by CLEEN, Cluster of Energy and Environment. The objective of the research is to build a strong mutual understanding of future business opportunities related to recycling of materials, as well as required know-how and abilities for their utilization. [35]

The background theory in the chapter 2 of the thesis gives a small review on the challenges and methods used in recycling of plastics and on the state of plastics recycling in the EU at the moment. The theory covers also the fundamentals of polymer miscibility and two compatibilization methods, that is, the non-reactive and reactive compatibilization. The next section of the background theory provides information on the equipment used in reactive compatibilization and explains the reactive extrusion steps of functionalization and compatibilization. The last section of the theory gives a review on the methods used in characterization of compatibilized polymer blends, such as morphological, mechanical and structural characterisation.

The third chapter Blends of polyethylene and polyamide is a small literature survey case study on the compatibilization of PE/PA blends. The first two sections describe the basic information on polyethylene and polyamide. The third section introduces the compatibilization methods used to compatibilize PE/PA blends and the last section focuses on the blends in which maleic anhydride grafted PE is used as a compatibilizer precursor and on the effects of the blend composition of this tertiary PE/PA/CP blend.

The fourth chapter explains the materials and methods used to prepare the samples and to characterize the compounds. In the fifth chapter Results and discussion the obtained results are presented and the observations are explained and discussed. The results are divided into five parts: visual observations, mechanical properties, morphological analysis and rheological and thermal properties. The last chapter summons the results and gives conclusions and recommendations on the possible sub sequential actions.

2. BACKGROUND THEORY

This chapter will cover the theoretical background for this work. The chapter is divided in to four parts: recycling of polymers, compatibilization of polymer blends, reactive extrusion and characterization of compatibilized polymer blends.

2.1 Recycling of Plastics

The recycling of plastic waste, that is, the process used to recover plastic waste is a hot topic as the demand of plastics keeps growing and the environmental awareness of consumers increases. The total plastic waste stream consists of post- industrial streams, that is, the off-spec parts, plant discards, and the like, and of post-consumer streams, that is, the municipal waste discarded after consumer use. The concept of recycling and recovering of plastics, however, often comprises only the post-consumer waste. [1]

This section covers the challenges met in plastic waste management and the technologies and practices in the industry. The last sub-section gives an insight into the recycling of plastics in the European Union at the moment and in the near future.

2.1.1 Challenges in recycling of plastics

Plastics are relatively inexpensive and versatile materials, which has led to exponential growth of the usage since their commercialization. This has led to different challenges in plastic waste management. The challenges can be divided into three categories: technical, economical and safety related challenges. The plastic waste streams consist of different types of plastics, and the products may consist of several different plastic typed melted together, and the products may be of different colour. All this demands proper sorting before successful melt processing is possible. As most of the main thermoplastics are immiscible with each other, an extra compatibilizer (see section 2.2) has to be added to the melt blend in order to achieve better properties. Also the contaminations in plastic waste, such as labels, glue, and printing, may cause difficulties in the recovery process. Other technical challenges can cause the variation of the thermal properties and processing parameters as the different melting points and melt flow rates may cause a mismatch in the final material. The economical challenges are in the high costs of waste transportation and reprocessing. The economics depends on the margin between the product price and the cost of raw materials as well as the size of the recycling facility. [1] Product safety sets challenges to the end-use of recycled materials as the additives and possible contaminations may limit the possible end-use applications.

Also the work safety of the people handling the plastic waste has to be taken into account. [36; 37]

The durability of plastic material is the biggest challenge with plastics. The material can overlive the product made of it and with the trends of growing demand the problem becomes bigger all the time. The uncontrolled disposal is problematic as plastics can persist the environment for a very long time. [38]

Especially plastic films are a difficult application for plastic waste management. Films do not usually have the identification code marked on the product, and to even complicate the sorting process, the films are often multilayer-structures by consisting layers of different polymer types. The additives in films may restrict the end-use of the recycled material. The volume-to-weight ratio of plastic films is relatively high and this increases the costs of transportation. [1]

However, plastic waste management is not only full of challenges, but also opportunities exist. The growth in the waste management industry, such as transporting and reprocessing, has a good opportunity also to generate new job opportunities. The improved technologies, waste management and product design will help to keep reducing the plastic waste produced. [38]

2.1.2 Plastic waste management

Waste management is based on *waste hierarchy*, in which the goal is to move up the hierarchy. On the highest position in the hierarchy is the most favoured option, prevention of waste. On the second place is preparing for re-use and after that recycling as a raw material. Other recovery, such as energy recovery comes second last just before actual disposal, which is the least favoured option. The hierarchy gives priorities when planning and managing recycling of any waste. [3]

Plastic waste management starts with the collection and sorting of the waste. In order to ease this process specific identification codes were launched in 1980s by Society of Plastic Industry, SPI. These numbered triangles are still used to identify the material used in plastic products. The labels and the corresponding plastic types are represented in Figure 2.1. [1]

Figure 2.1 SPI identification codes for different plastic types. Adapted from [1]

Reclamation and recycling of plastics can be done in multiple ways. The main methods are reuse, mechanical recycling and chemical recycling. *Reuse* is not so common with plastic waste, especially in relation to plastic packaging. However, some exceptions exist, such as the detergent bottles that can be refilled with a separate refill sachet. As the material that is recovered within the same manufacturing process that generated it does not count as recycled material the post-industrial waste has to be recovered outside the manufacturing process, such as by another company that buys this post-industrial waste for feedstock [39]. The use of the scrap and offcuts within the same manufacturing process is part of the good manufacturing practice, GMP. The use of the regrind post-industrial waste as a blend component with virgin material is classified as the most straightforward approach to recycling. In *mechanical recycling* the sorted or non-sorted post-consumer waste material is ground down in order to reprocess and compound it. The product of the reprocessing may or may not be the same as the original use of the material. C*hemical recycling* involves thermal treatments, such as pyrolysis or hydrogenation, in order to turn the polymer waste back to its monomers or hydrocarbon components. These components can be then used as raw materials for new polymers. [1; 40]

2.1.3 Recycling of plastics in the European Union

In 2013 about 57 million tonnes of plastic was produced in the 27 member states of the European Union, EU. Packaging applications have the largest demand for plastics, about 40% of the total plastic demand in the EU. The two next biggest applications are building and construction applications and automotive applications with shares of 20% and 8.5%, respectively, of the total demand. When different plastic types are compared, takes polyethylenes, that is, high density polyethylene, HDPE, low density polyethylene, LDPE and linear low density polyethylene, LLDPE, the greatest share of the total demand, almost 30%. Polypropylene, PP and polyvinyl chloride, PVC are the second and the third most used polymers in the EU. [2]

In 2012 over 25 million tonnes of post-consumer plastic waste ended up in the waste upstream for recycling or disposal. As Figure 2.2 shows, 62% of the waste was recovered by recycling or by energy recovery and thus, 38% of the plastic waste went to landfills. The share of plastic waste ending up in recycling has increased by 40% between 2006 and 2012. In 2012 6.6 million tonnes of plastic was recycled, which was 26% of the total amount of plastic in waste upstream. [2]

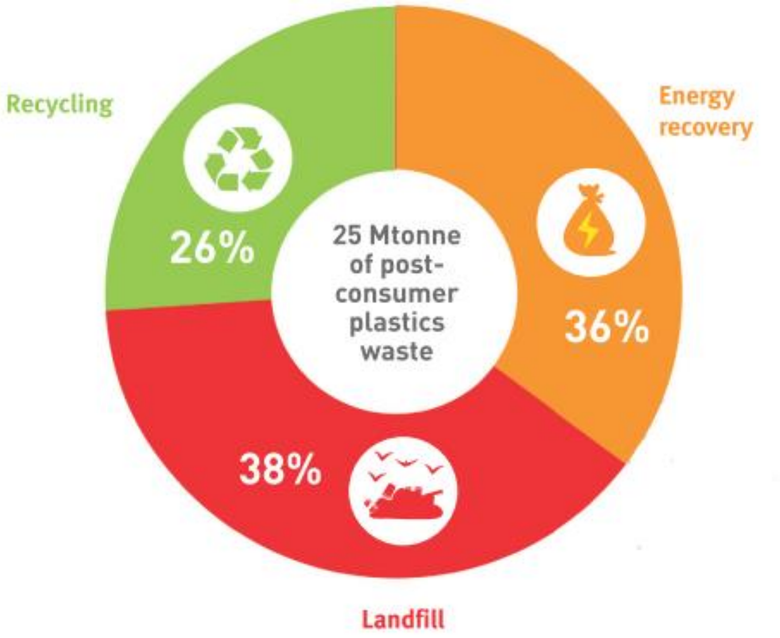


Figure 2.2 Treatment for post-consumer plastics waste in 2012 in EU member states+Norway and Switzerland. [2]

In some countries, for example in Sweden, Norway and Germany, it is banned to send the plastics waste to landfill, and for example in Finland and in Poland this ban comes in force in 2016. At least in Finland the landfill ban of plastics is a part of a larger landfill regulation prohibiting the waste with more than 10% of organics waste going to landfills [41]. However, in some countries, such as in United Kingdom and Greece still above 66% of plastics waste goes to landfills. In 2011 the European plastic industry launched the initiative ‘zero plastic to landfill’. The initiative aims to reduce the plastic waste going to landfills to zero by 2020. The goal is challenging, as the extrapolated trend lines suggest that the zero goal will not be reached before 2037, as represented in Figure 2.3. [2]

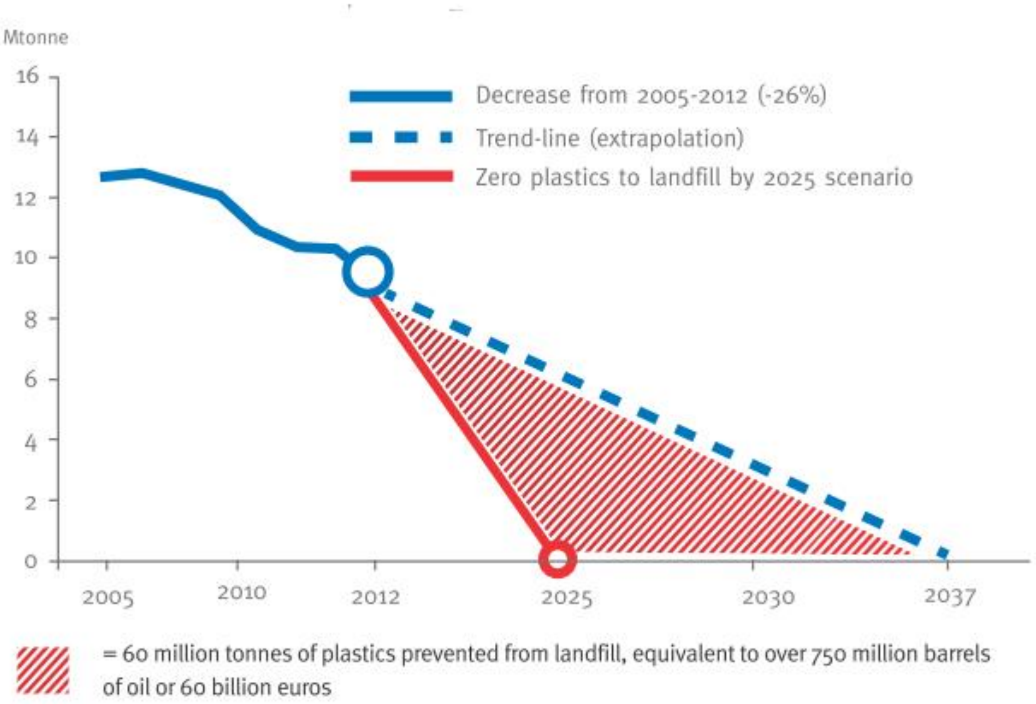


Figure 2.3 Plastics waste going to landfill in Europe [2]

The plastic waste management is regulated in European Union by local laws and regulations covering the whole EU and the landfill bans are a good example of the differences between the local regulations. The European Union legislation does not specifically address plastic waste despite its growing environmental impact – only the Packaging Directive 94/62/EC [42] has a specific recycling target for plastic packaging. Some relevance gives the Registration, Evaluation, Authorization and Restriction, REACH, Regulation 1907/2006/EC [43] which regulates for example the placing on the markets of the recycled materials. This means that for example some additives in recycled resins may no longer be allowed in new products if they do dot compliance within REACH for example by the exceeding concentration. [38]

The international standards apply also in the European Union. For example the International Organization for Standardization, ISO, has a standard ISO 15270:2008, Plastics – Guidelines for the recovery and recycling of plastics waste [44], which establishes different options for the recovery of plastics waste arising from pre-consumer and post-consumer sources. It also establishes the quality requirements that should be considered in all steps of the recovery process, and provides general recommendations for inclusion in material standards, test standards and product specifications. The European Standard, SFS-EN 15343, Plastics - Recycled plastics. Plastics recycling traceability and assessment of conformity and recycled content [39] gives, for example, the basis for the calculation procedure for the recycled content of a product.

2.2 Compatibilization of polymer blends

Many thermoplastic polymers are immiscible with each other and this leads to phase separated structures. These structures can be restabilized by using specific interfacial agents, compatibilizers. [5] This section elaborates the miscibility of polymers and the reasons, why to compatibilize. It also gives examples of common nonreactive and reactive compatibilization methods.

2.2.1 Miscibility of polymers

Mixing of different polymers together in various proportions makes it possible to achieve new final materials with a range of property combinations [7]. This is also usually more cost-effective method than synthesizing a new polymer. However, most of the thermoplastics used are immiscible with each other [1]. For example the mechanical recycling of multi-layer plastic film is not possible if pure material is needed as the layers of different polymers are attached to each other. In this case it is possible to melt the scrap and use it as a blend as the separation of the layers from each other may be extremely difficult.

Mixing of polymers, however, is not a simple task as the general rule “like dissolves alike” does not always comply with polymers. Usually, the total miscibility of two or more polymers is defined by the formation of a one-phase system and this depends on entropy and enthalpy of the system. In polymer-polymer systems the factors affecting entropy and enthalpy of mixing are, such as, the structure of the mixed polymers and the presence of functional groups in polymer molecules capable of mutual interactions [45; 46].

One method used to assess the miscibility of polymer blend is to calculate the Flory-Huggins interaction parameter χ. The smaller the parameter is, the more miscible the blend is. The factors affecting this binary thermodynamic interaction function are for example concentrations, molecular weight and molecular weight distribution of the interacting molecules and different processing conditions such as temperature and pressure [47]. The interaction parameter is often related to solubility parameter δ, by using the difference between the solubility parameters of the mixed components (δ_1 and δ_2) according to following equation:

$$\chi = \frac{v_1}{RT}(\delta_1 - \delta_2)^2, \tag{1}$$

where v_1 is the molar volume of the solvent and R the ideal gas constant. The solubility parameter, δ depends on the molar attractions inherent in the component. The Flory-Huggins theory predicts that it is almost impossible to find a miscible polymer pair in absence of any specific interactions. Thus, the δ_i values for the components of a blend would to have to be closely matching in order for the blend to be miscible. [45; 47]

As the difference between the solubility parameters of the polymer components in a blend becomes too big, or when the interaction parameter of the mixture is too high the mixture is no longer miscible and two separate phases are observed. This is normally due to the interfacial tension between the components as the interfacial adhesion is low. This phenomenon is not totally undesired but immiscibility or partial immiscibility of polymers enable formation of a wide range of structures. As the low interfacial adhesion between the phases usually results in poor mechanical properties in the final material the stabilization of the phase structure against minor phase coalescence may result in excellent end-use properties. The stabilization can be done by using an interfacial agent, that is, a compatibilizer, to reduce the interfacial tension to suppress phase separation and improve adhesion. The compatibilizers modify the interface by forming chemical or physical bonds between the polymers. [5]

Compatibilization of polymer blends does not necessarily make the blend miscible but phase separation may still occur. Via the decreased surface tension the droplets of the dispersed phase are finer and stabilized. The compatibilizers usually contain parts that are miscible with the matrix and other parts miscible with the dispersed phase, such as graft or block copolymers. The copolymers act at the interface by interpenetrating from one phase to another and anchor the phases together. A schematic representation of different types of copolymers acting as compatibilizers at polymer-polymer interfaces is represented in Figure 2.4. [5; 48]

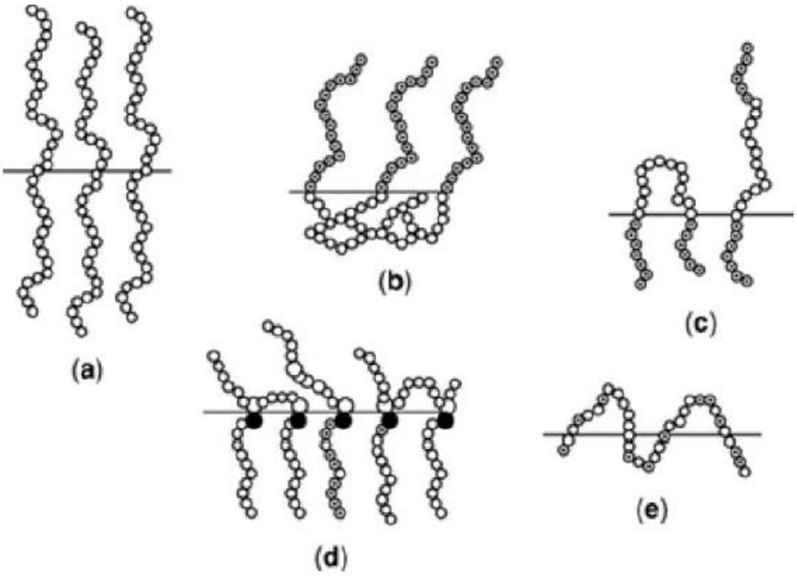


Figure 2.4 Different copolymer compatibilizers at the interface: a) diblock copolymer, b) end-grafted chains, c) triblock copolymer, d) multiply grafted chain and e) random copolymer [5]

In general, the compatibilization of a polymer blend should accomplish:

a) optimization of the interfacial tension,
b) stability of the morphology against high stresses during subsequent processing and
c) enhancement in adhesion between the blend components in solid state. [49]

The compatibilizer can be introduced into a polymer blend in two ways: by synthesising a suitable copolymer and then melt blending it with the polymer blend that need to be compatibilized, or by combining reactively some portions of the different polymer components of the blend during melting. The former method is also known as non-reactive compatibilization and the latter as in-situ reactive compatibilization. [48]

The next two sub-sections describe different non-reactive and reactive compatibilization methods that are used in general for compatibilization of polymer blends.

2.2.2 Non-reactive compatibilization

The non-reactive compatibilization involves no chemical or physical reaction between any blend components during compounding or processing but the compatibilizing effect occurs with the components already present in the blend. The most common non-reactive compatibilization method is *addition of block or graft copolymers*. These pre-synthesised polymers are designed so that one segment is miscible with one blend component and another segment is miscible with the other blend component. The segments are not necessarily exactly identical with the respective polymers but the miscibility with the blend component is what counts. In addition to blend composition and processing conditions the molecular weight and architecture of the compatibilizer, that is the type, number and molecular parameters of segments have an effect on the morphology and properties of the final material. For example, random copolymers can act as a compatibilizer but their ability to stabilize the structure is limited. [5; 50]

One disadvantage for the addition of block or graft copolymer is that the method requires a specific copolymer for each different polymer blend. This may require complex and costly synthesising processes and it adds an extra step to the whole compounding process. In the blending process significantly higher amounts of compatibilizer might be needed as some parts of the copolymer may get trapped in the matrix phase during blending and never reach the interface [5]. Also the tendency of the copolymers to form micelles and the effects of large copolymers on the flow properties of the melt blends are limitations for this method [49].

The utilization of nonbonding specific interactions is another non-reactive compatibilization method. In general the principle is to affect the polarity of the blend components and thereby change the enthalpy of mixing. In addition, a drop in the interfacial tension and an increase in the interphase thickness can be observed. The blend components can be modified, for example, by grafting functional groups onto the original polymers. [51] The specific interactions, such as: hydrogen bonding, ion-dipole and dipole-dipole bonds are weak bonds and therefore the effective compatibilization would need relatively high concentrations of the compatibilizer polymer in the blends which may change the properties of the end product [50].

2.2.3 Reactive compatibilization

In reactive compatibilization method the compatibilizer is formed in situ during the blending or processing by formation of new graft of block copolymers, by crosslinking or by using other additives. The general principle is to reactively combine some portion of the different polymer components in the blend during melt processing and thus generate a stable morphology and modified interfacial properties with finer structure and improved mechanical properties of the final material. [48]

When compared to non-reactive compatibilization reactive compatibilization method has at least one processing step less as the compatibilizer is formed in situ during the melt processing and no separate step for synthesis of the compatibilizer is needed before the blending. Also the structural control of the compatibilizer in the reactive method is easier. Because the compatibilizer is generated where it is needed there is no problem of transporting the copolymer to the interface and thus, less compatibilizer is needed. It has also been suggested that the reactive blends have thicker interphase than non-reactive blends with added copolymers and therefore a reactively compatibilized blend has higher stability during subsequent processing. [48; 49; 52; 53]

The most common method for reactive compatibilization is *addition of reactive polymers*. The method deploys a third blend component, that is, a reactive polymer that is miscible with one blend component and reactive towards functional groups attached to the second blend component. As a result a block or graft copolymer is formed in situ. This reactive polymer is often called a compatibilizer precursor, CP because the final compatibilizer is formed when the final block or graft copolymer is formed. However, the term compatibilizer is in many occasions used also just for the reactive polymer. [51]

Reactive polymers are usually generated by modifying chemically inert polymer chains with no inherent functionality, such as polyolefins. The functionalization of polyethylene has been covered more comprehensively in section 2.3.2. In some cases, when neither of the phases contain reactive groups inherent in the polymer, both phases have to be functionalised. The functional groups used to form inter-chain copolymers must have suitable reactivity in order to react across the melt phase boundary during the short blending time and the generated bond must be sufficiently stable to survive subsequent processing conditions. The majority of the used functionalities have electrophilic nature, such as carboxylic acid, cyclic anhydride, epoxide, oxazoline and isocyanate, and these can react with nucleophilic groups normally inherent in the polymer such as amine or carboxylate groups. [50-52] Some common compatibilization reactions, that is, the in situ formation of the copolymer are reviewed in section 2.3.3. In that section more practical examples are also given.

Another reactive compatibilization method *is the addition of low-molecular weight reagents*. The method is suitable for polymer blends in which none of the polymer components contain functional groups for chemical reactions, such as blends of polyolefins or for blends in which functionalization of the other component is needed. The purpose is to graft a low molecular weight functional reagent onto the inert polymer in situ and thus form the compatibilizer or to use free radical initiator, such as peroxide to activate the inert polymer and to generate copolymers directly between the blend components. For these systems free radicals or combination of free radical initiator and a suitable low-molecular weight co-reagent, such as maleic anhydride, multifunctional epoxy monomers and organosilanes can be used [50]. This method results in better adhesion between phases and/or better stress distribution in the solid state morphology when material is under stress [48]. For example Lambla and Seadan [54] were able to form in situ compatibilizing graft copolymers without any premade reactive polymer by adding peroxides into the blend of polyethylene and polyamide. The reactivity was even enhanced when adding maleic anhydride monomers as co-reagents. [48]

Other reactive compatibilization methods are for example vector fluid concept that deploys a fluid that locates preferentially at the interphase between the blend components. This fluid can then carry different reactive ingredient such as peroxides where they are needed to compatibilize the system. Also the introduction of free radicals initiated by mechanical shear forces may result in recombination of different polymer components or addition to unsaturated bonds. [48; 51; 55]

A novel approach for reactive compatibilization has been presented by Hu, Cartier and Plummer [53; 56] who were able to synthesise one blend component in situ in presence of another blend component and simultaneously form in situ a compatibilizer by initialising the original blend component sites from which the new component can grow. This method was shown to result in a fine, nanometer-scale morphology.

2.3 Reactive extrusion

Reactive extrusion, as the term suggests, involves the synthesis of a new material by a melt phase reaction is situ, in the extruder during melt processing [57]. The traditional compatibilization process may be divided into three stages:

1. Generating the reactive polymer, for example by grafting functional groups onto the main chain,
2. Generations of the graft or block copolymer, i.e. the compatibilizer, and
3. Compounding thus formed copolymer with a mixture of neat polymers.

With reactive extrusion the steps are possible to reduce into two or even into a single step due to the developments in the technology during the last decades. [49]

When compared to the alternative technologies reactive extrusion allows solvent-free processing and simple product isolation in a continuous process and with relatively low infrastructure costs. The challenges in reactive extrusion are the need of a sufficient mixing of components and the requirements of high temperatures to melt the processed polymers. Also the extent of unwanted side reactions, that is for example cross-linking, and chain scission that may accompany processing can cause problems if not controlled. [57]

The following sub-sections cover the descriptions of reactive extruders as chemical reactors and reactive extrusion process and also describe the chemical processing steps of functionalization of polyethylene and the different compatibilization reactions.

2.3.1 Screw extruder as chemical reactor and reactive blender

As a chemical reactor a screw extruder is considered to be a continuous flow reactor [58]. Normally an extruder consists of a long cylinder, the barrel, and inside it locates one or two screws and at the end of the extruder is a die which gives the form for the molten polymer pushed through it [59]. The external openings in different barrel segments are typical for reactive extruders. The openings enable the introductions of solid, liquid, or gaseous reactants at specified points in the chemical process [60]. A schematic example of a reactive extruder is given in Figure 2.5.

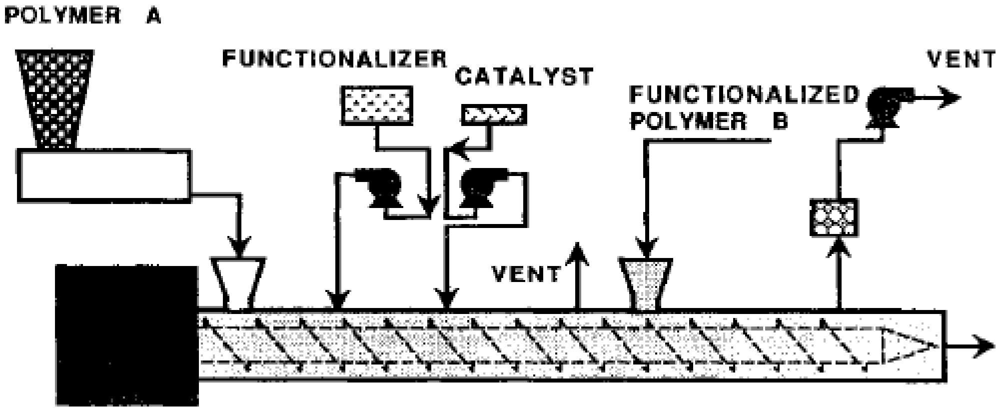


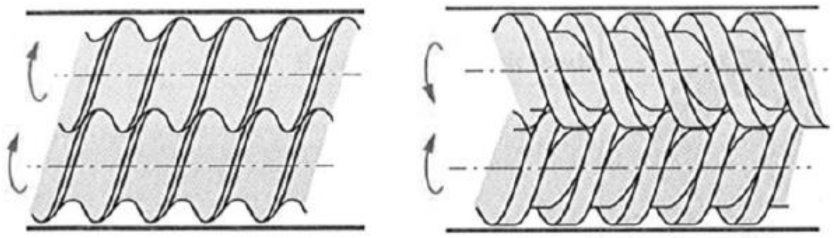
Figure 2.5 Schematic of a sequential functionalization / blending operation in extrusion equipment [55]

The advantage of a reactive extruder as a chemical reactor is the combination of several chemical process operations into one piece of equipment with accompanying high space-time yields of product. Operating conditions vary between 70-500°C and the residence time is usually between 10-600 s. and, hence, the time available for a chemical reaction, is determined by extruder length, free volume inside the barrel, the rate of introduction of reactant, and screw speed. [60]

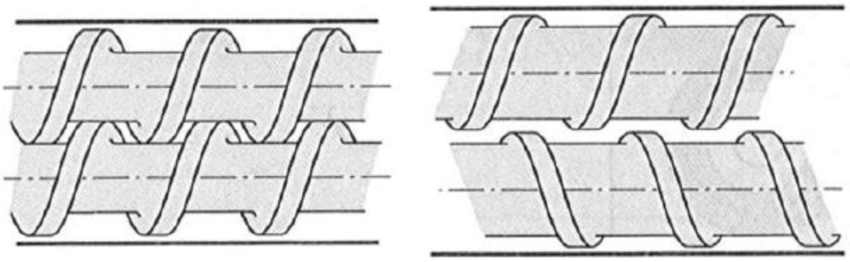
An extruder may be considered to be a horizontal, tubular reactor due to its lengthwise geometry with one or two internal screws for conveying and mixing reactant polymers or monomers. The laminar flow pattern makes it possible to perform various operations in a sequential manner, such as feeding, conveying, melting, mixing, reacting, venting, pumping and shaping. The screws in the reactive extruders usually have specialized sections or configurations, for example high shear mixing section. By varying the external heating, the screw element configuration, and the clearance between screw and barrel wall it is possible to vary the individual barrel segments, the total energy and degree of mixing in each sectors. This makes reactive extruder a chemical reactor with individually controlled reaction zones. [58; 60]

Because of the unique transport mechanism the chemical reactions occur in molten polymers without any solvent as the reaction medium. This is an advantage when compared to the traditional reactors as no solvent stripping or recovery process is required. Because of the versatility, most extruder reactors are twin screw extruders, which possess a segmented barrel, each segment of which can be individually cooled or heated externally. The shear induced heat also usually enhances the chemical reactivity of the processed substances. [60]

The main differences between single and twin-screw extruders are in the transport mechanism and in the flow patterns in the machines. A single screw extruder has a drag-induced material transport, that is, the frictional drag in the solids conveying zone and viscous drag in the melt conveying zone, whereas in a twin-screw extruder the transport mechanism is by a positive displacement. In an intermeshing twin-screw extruder the two screws are interpenetrated and the degree of the positive displacement depends on the degree of this intermeshing. Interpenetrated and non-interpenetrated screws are presented in Figure 2.6. [58]



Co-rotating screws **Counter-rotating screws**



Interpenetrated screws **Non-Interpenetrated screws**

Figure 2.6 Classification of twin-screw systems [58]

There are two types of twin-screw extruders, co-rotating and counter-rotating extruders. The difference between these types is obviously in the rotation direction of the two screws and thereby in the flow of the polymer melt inside the barrel [58]. Both screw types are used in compounding but based on the literature survey the co-rotating screw is more commonly used in reactive extrusion.

Single-screw extruders are considered to have low cost, straightforward design, ruggedness, high throughput and mechanical reliability. However, twin-screw extruders are thought to outperform single-screw extruders because of the versatility of the process: it has better feeding and transport characteristics, better control over residence time and the mixing is more efficient. The larger surface/ volume ratio affects the mixing area, melting capacity and the devolatilization capacities that are all larger than in single-screw extruders. Thus, altogether, the flexibility of the process is greater and this owes to the modular design of the twin-screw extruders. [58]

A typical *reactive extrusion process* involves several functions: The reactants are fed into the extruder and material is heated to initiate the reaction or to increase the reaction rate. The reactant mixture is all the time conveyed through the barrel in order to achieve sufficient mixing and specific energy input. The aim is to reach a desired degree of completion with the chemical reactions within the limits of residence time. The reactions are quenched by cooling or addition of a catalyst quencher. The volatile by-products or excess reactants may be removed through the specific devolatilization channels. Molten polymer is then forced from the extruder through a die and any still occurring chemical reactions are quenched by cooling and solidification. [60]

For optimum operation, an extruder reactor must be custom designed with specific knowledge of the type of chemical reaction desired. A sufficient dispersive and distributive mixing is one of the fundamental requirements for reactive extrusion process as it ascertains the required renewal of the phase interface. However, the ultimate morphology, that is, the size of the dispersed phase droplets, is almost independent of the rotation speed of the screw as it affects mostly on the chemical conversion rate [61]. The flow generated by mixing has been shown to affect the interfacial reaction rate and it has been demonstrated that the rate constants in mixed heterogeneous systems were 1000 times higher than in static bilayer systems [62; 63]. The different screw configurations are the solutions for this problem. Because the residence time also sets limitations to the reaction, the length of the extruder and the screw configurations have to be selected carefully. [49; 60]

The effects of processing conditions on the chemical conversion and morphology evolution have been studied for example by Yquel at al. [33]. A modular, intermeshing, corotating twin screw extruder was used to study the evolution of the morphology of PA/PE blends with PE bearing MA species along the extruder. In their work Yquel at al. demonstrated, that the melting stage, in terms of both the location of its onset and its development rate, greatly influences the chemical conversion and the morphology evolution of a fast reactive compatibilization system. The study also showed that increasing screw speed or using more restrictive screw modules at the beginning of the melting zone promotes faster reactions and better dispersion along the extruder and thus they have a strong effect on the distributive and dispersive mixing rates and intensity. Also, increasing the throughput was shown to slow the evolution of the blend morphology and decreasing the barrel temperature delays the blend compatibilization due to the slower melting. [33]

In order for the reactive compatibilization process to result in stabilized chemical and morphological structures the blend components have to be chosen carefully. The presence of functionalities in each phase is a must, no matter if the functional groups are inherent or originate from in situ functionalization. The suitable functional groups are limited by the reactivity as the reaction must take place within the residence time. [49]

2.3.2 Functionalization of polyethylene

The functionalization of polyethylenes and the synthesis of functional polyethylenes have been studied widely. Comprehensive reviews have been written for example by Cuang [64], Moad [57], Passaglia et al. [65] and Yanjarappa and Sivaram [66]. Polyolefins and especially polyethylenes have been proven to be preferred substrates for reactive extrusion experiments. This may be largely attributed to their ready availability and widespread commercial applications [57].

There are some molecular features that are characteristic for a reactive polymer: It contains a functional group capable to react with other functional groups present in the blend. The type, concentration and distribution of the functional group all affect the reactivity and the reaction kinetics. [67]

In general, the synthesis of functional polyethylenes may be divided into two categories, namely, chain end functionalization and in chain functionalization. The former method involves functionalization of preformed terminally unsaturated polyethylenes, whereas, the latter method involves the copolymerization of polyethylenes with comonomers having the desired functional group. Most of the methods deploy free radical initiators and especially the copolymerisation process is limited by the ability of many functional groups to coordinate with the catalyst or co-catalyst components. [66]

As an option for direct synthesis of functional polyethylenes there are post-polymerization functionalization actions. Preformed polyethylene chains may be functionalized before blending process in a separate processing step by solution grafting, melt grafting, solid state functionalization, copolymerization, end-capping, physical procedures, surface functionalization, mechanochemical functionalization and others. [6]

The most widespread method of introducing functionality into polyethylene substrates in reactive extrusion process involves free radical-induced grafting onto preformed polyethylene chains. The process generally involves combining a free radical initiator and a monomer or macromonomer with the polyethylene as it is conveyed through the extruder. The most commonly used initiators are peroxides although, other initiators have also been used, such as shear induced free radicals or ionizing radiation. [57]

In general, the functional groups must be stable enough under the process conditions to withstand high temperature and exposure to air and humidity [68]. A wide range of monomers and macromonomers have been successfully grafted onto polyethylene substrates that fulfil this requirement. Common moieties used in functionalization of polyethylenes are for example maleic anhydride, MAH or MA, methacrylates, oxazoline, vinyl silane, and maleates and fumarates. Grafting MAH onto PE is one of the most studied reactions of polyethylene modification processes, probably due to the popularity of MAH as a coupling agent in compatibilization reactions. Glycidyl methacrylate, GMA is an ester of methacrylic acid and provides epoxy functionalization onto PE chains and it has been used widely as an in situ compatibilizer in blends of polyolefins and polyamides or polyesters. [57] Oxazoline is a more recent discovery as a reactive functional group used in reactive extrusion. Long chain oxazolines have been reported to be less toxic than MAH and GMA, and their boiling points are well above those of MAH and GMA [69].

Burgstaller et al. [9] presented a schematic illustration of a simplified example reaction between maleic anhydride and polyethylene when grafting MAH onto PE by radical initiator. In Figure 2.7 the first line represents the initiation reaction for forming two free radicals. On line two, the free radical is transferred to the polyethylene chain. The MA grafting onto PE and the formation of a new radicalized PE chain are presented on the last lines.

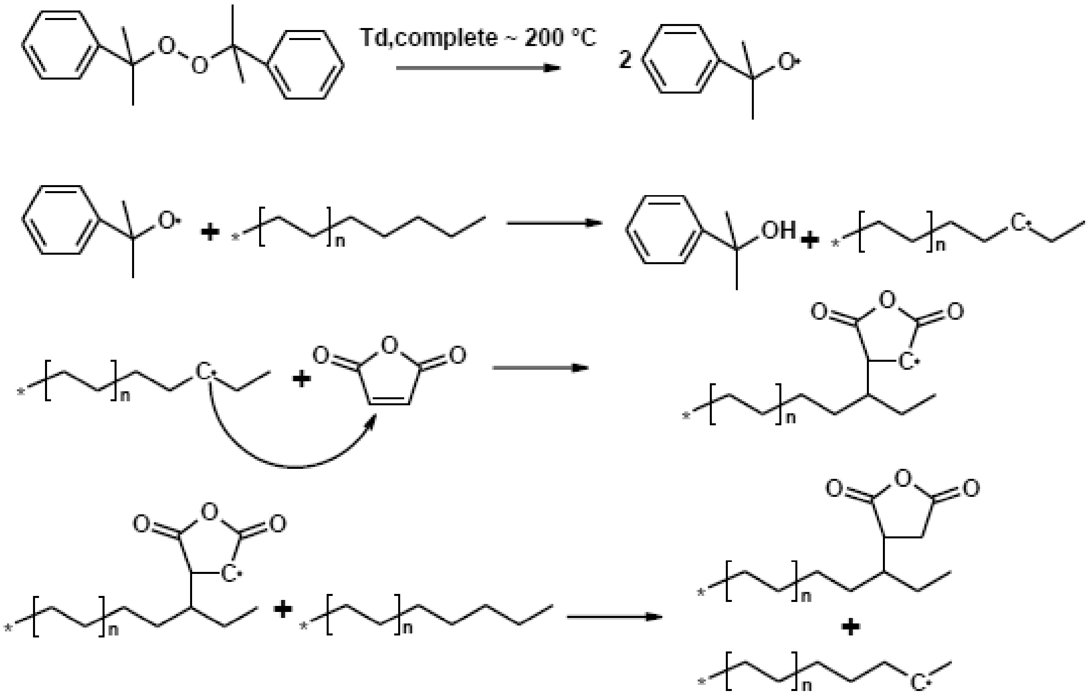


Figure 2.7 Schematic presentation of the reaction between MA and PE chain enabled by radical grafting [9]

The radical induced grafting of functionalities onto PE and ethylene copolymers is usually accompanied with different side reactions, such as

a) radical induced crosslinking of the polyolefin substrate, which leads to the formation of gels and increase in torque
b) radical induced chain scission of the polyolefin substrate,
c) shear induced degradation of the polyolefin substrate and
d) homopolymerization of the monomer. [57]

However, by the optimization of the processing parameters the extent of these side reactions can be minimized [57]. In some cases the crosslinking may be even totally avoided and a completely soluble product is provided and still very high grafting yields can be obtained [9].

There are many factors in reactive processing affecting *the grafting yield*, that is, the fraction of the monomer that is grafted onto the polymer versus that which is either unchanged or is consumed in side reactions such as homopolymerization. The processing related factors include such as mixing efficiency, temperature, pressure, residence time, venting or the design of the screw or the extruder. Also the blend composition related factors, such as the selection and concentration of the base polymer, monomers, initiator and co-agents. [57]

Chuai et al. [70] reported on the increasing grafting degree with increasing free MAH concentration as they studied the melt grafting of maleic anhydride onto LDPE. Their results showed a systematical increase up to 5.1% of grafting with MAH content of 0.14 wt.% and above that the grafting degree showed a linear decrease. Chuai et al. suggested that the chemical reactions for the grafting almost terminate at 0.14 wt.% if the thermal degradation is neglected. In the same study it was also shown that the peroxide initiator concentration up to 0.45 wt.% results with increasing grafting degree and beyond that the degree starts to drop. They suggested, that this phenomenon directly demonstrates that when high concentration of the initiator is added to the reaction mixture, the rate of generation of free radical species reaches such a high value that the homopolymerization of MAH becomes more significant and thus depressing the grafting process. Also the grafting temperature was shown to have an effect on grafting degree and the highest degree resulted at 160°C.

In reactive extrusion the monomer can be added simultaneously with the polyolefin or it can be added to the molten polyolefin directly, adsorbed on further polymer, or be dissolved in an appropriate solvent. The best method depends on the solubility of the monomer in the polyolefin melt and the stability and volatility of the monomer. Initiators used in the process have to be selected carefully for the grafting experiment. Most commonly initiators are dialkyl peroxides but also other initiators are used. The method of introducing the initiator also affects the selection and the extent of side reaction and the formation of initiator derived by-products. The susceptibility of the initiator to induced decomposition and other side reaction is to be taken into account. [57]

As the architecture of the reactive polymer affects its ability to act sufficiently as a compatibilizer, at least three aspects of the structure of the maleated polyethylene need to be considered:

a) The nature of the anhydride functionality that is the possibility of oligo-MAH grafts or adjacent grafts.
b) The distribution of the anhydride functionality along the polyolefin chain and between chains (typically 0.5-2 wt.%, which basically means only about one or two units per chain).
c) The relationship between the nature, distribution and level of grafted functionality, and other aspects of polyolefin structure (e.g. molecular weight, polydispersity, density or degree of branching). [57]

In studies by Heinen et al. [71] it was shown that the MAH may be attached to polyethylene backbone at methine sites (Figure 2.8a) or at methylene sites (Figure 2.8b and c).

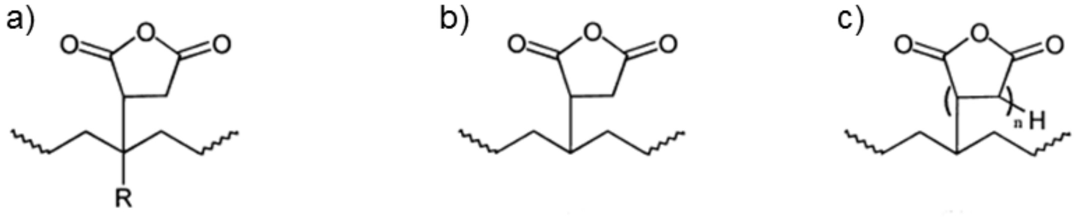


Figure 2.8 Scheme of possible sites for MAH to be attached at a) methine site, b) and c) methylene sites. [57]

Their work suggests that grafted MAH appears dominantly as oligo(MAH) blocks in HDPE (Figure 2.8c) with chain length of the oligo (MAH) averaging between one and two units, and in LLDPE both oligo(MAH) at methylene sites and succinic anhydride units at methine sites. The same results were obtained by Ranganathan et al. [72] who also reported that the distribution of the MAH-residues at tertiary methine sites was random.

2.3.3 Compatibilization reactions

The compatibilization reaction, that is, the in situ formation of copolymers between the blend components is an essential step in reactive compatibilization process. When polyolefins, and in this case polyethylene especially, are considered, these inter-chain polymer reactions can be divided into three categories based on the type of the structure of the component reacting with modified, namely, the reactive polyethylene.

The first class is *end-functional polymers with reactive polyethylene*. Normally the product of this reaction is the formation of a graft copolymer. A major limitation for this compatibilization reaction is the commercial availability of end-functional polymers. Most of these are condensation polymers which by their nature have potentially reactive end-groups, such as, polyamides with amino and/or carboxy end groups, polyesters and polycarbonates with hydroxyl and carboxy end groups and polyethers commonly with hydroxyl end groups. However, the end group functionality also depends on the processing history and with commercial products the available functionalities are not necessarily specified. [57]

Polyfunctional polymers with multiple side chains reacting with modified polyethylenes are the second class. These reactions have been used to synthesize graft copolymers, but due to the polyfunctionality of both substrates, also cross-linked products can be generated. The cross-linking can be avoided by careful selection of substrates and control of processing conditions. For example, copolymer of vinyl and styrene with oxazoline moieties have been used in blends with modified polyolefins. [57]

In the last class are *the reactions between polyethylene and another polymer by using a coupling agent*. The coupling agent forms linkages between the polymer chains and an in situ synthesis of a graft copolymer may occur. The reactions usually require peroxide initiator and possibly a polyfunctional monomer as a coupling agent. [57]

The variation of the formed compatibilizer structure is also represented in Figure 2.9. Compatibilizer with end reactive functional groups can form block copolymers with another blend component containing also end reactive groups (Alternative I) and graft copolymers with a blend component with inherent pendant groups (Alternative II). An addition of reactive polymer carrying pendant reactive groups may generate grafted copolymers (Alternative III) or branched copolymers (Alternative IV). [51]

The three important things to be taken into account when considering the controlling of the copolymer formation at the interfaces are the chemistry of the blend components, the kinetics of the reactions and the architecture of the forming copolymer. *The chemistry* of the blend includes the chemicals involved in the compatibilization reactions and the new bonds formed between the components. All the components should sustain the processing environments and meet the health and safety regulations. [61] The functional groups in the components determine the possible reactions, and in order for successful compatibilization reactions to occur the reaction should be fast, selective and preferably irreversible. Functional groups with a capability to take part in these type of reactions, and react with the functionalised compatibilizer precursors, are such as maleic anhydride, carboxylic acid, primary and secondary amines, hydroxyl groups, heterocyclic groups and groups with interchange reaction or ionic interaction capabilities. [50]

Figure 2.10 represents some examples of functional groups taking part in compatibilization reactions and possible chemical bonds that may form. The reactions are classified by the functionality of the compatibilizer precursor (X, left hand side column) and possible functional groups that are able to react with the CP (Y, mid-column). The right hand side column in Figure 2.10 represent the bonds forming between the functionalities X and Y, X’-Y’.

Most of the compatibilization reactions are condensation reaction between a nucleophilic end group (that is, electron donor, for example -NH_2, -COOH, and -OH) and an electrophilic group (for example cyclic anhydride, epoxy, and isocyanate). The resulting reaction is usually a formation of new chemical groups, such as imide group in the reaction of cyclic anhydride and amine, or ring opening reactions such as in reaction between epoxy and carboxylic acid or oxazoline and alcohol. [6]

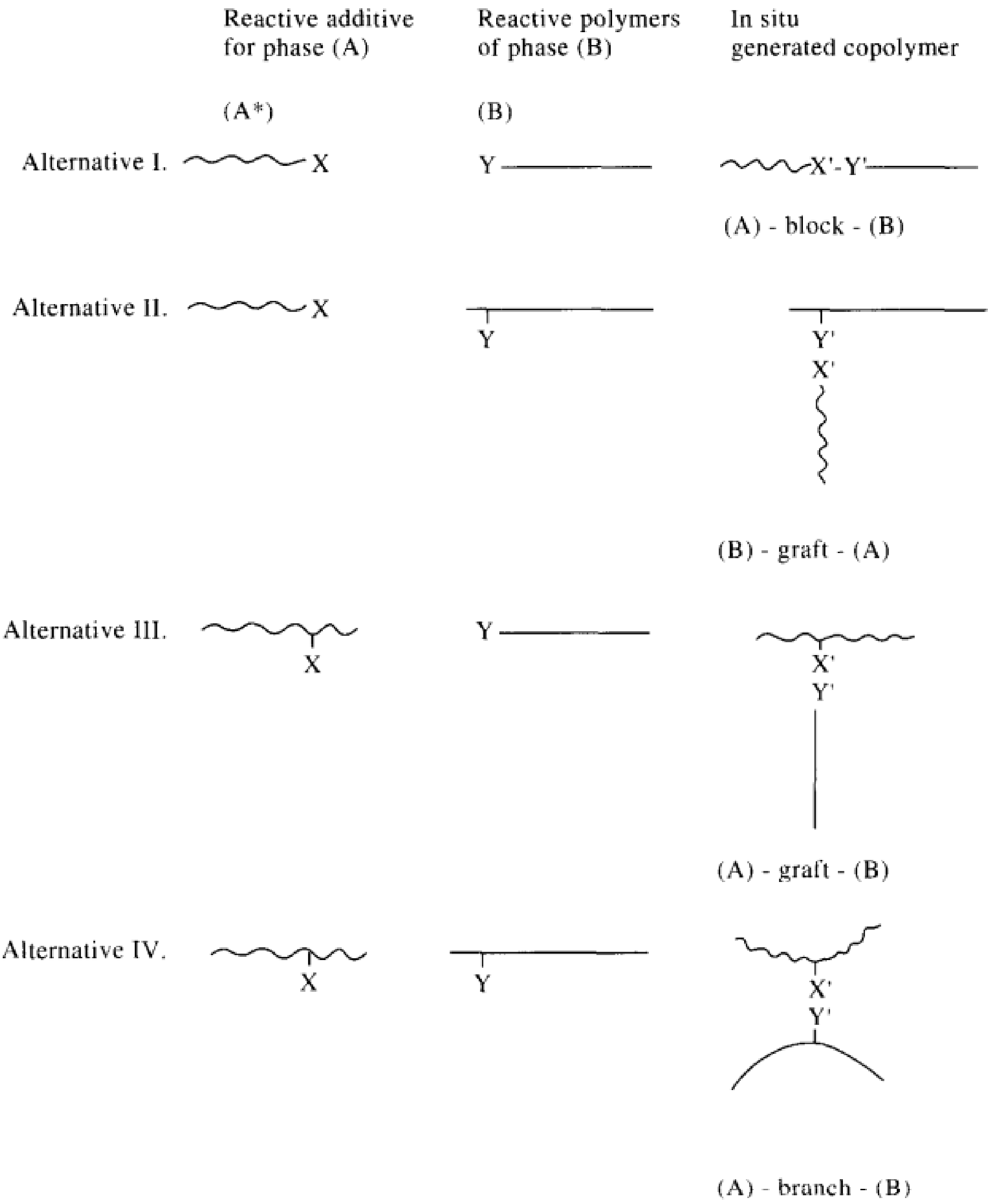


Figure 2.9 Types of copolymers formed during reactive processing [51]

Reaction kinetics, that is, the rate of inter-chain copolymer formation is affected by the inherent reactivity of the components and the functional groups involved. The kinetics depends on the interfacial area available and thus sufficient mixing is of importance. By selecting a suitable functional group pair with sufficient reactivity the conversion rates are possible to keep within the required limits of reactive processing. However, the determination of the reactivity can be difficult. [61; 63]

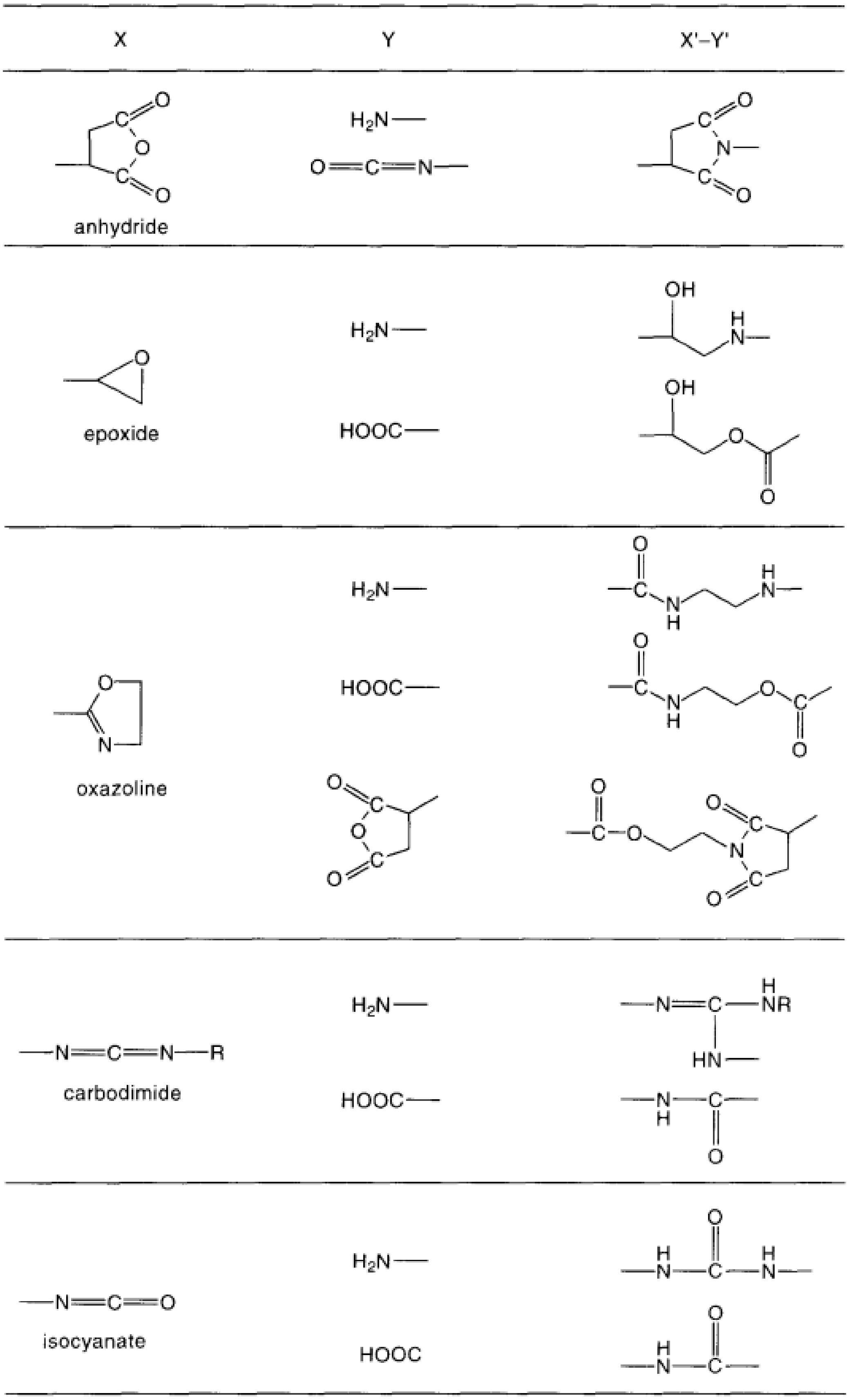


Figure 2.10 Reactive groups involved in reactive processing [51]

The reactivity of specific functional group pairs were studied by Orr et al. [73]. They measured homogenous coupling kinetics of terminally functional polymers by attaching a variety of functional groups to the end of polystyrene, PS and polymethyl methacrylate, PMMA. In order of increasing reactivity, functional group pairs are: acid/amine, hydroxyl/(anhydride or acid), aromatic amine/epoxy, aliphatic amine/epoxy, acid/oxazoline, acid/epoxy, aromatic amine/anhydride, and aliphatic amine/anhydride. [73]

One factor affecting the reactivity and reaction kinetics is the *architecture of the reaction components*, namely, the compatibilizing efficiency is closely related to the location and amount of reactive groups. However, the architecture is often unknown or difficult to control. [61] The reaction rate constants for different end-functional and mid-functional chains were studied by Jeon et al. [62]. They compared the reactivity for an end-functional chain reacting with and an end-functional chain versus reacting with a mid-functional chain by using competitive reactions of end- and mid-functional phthalic anhydrides with amine groups. It was found that the mid-functional reaction was slower to react under all reaction conditions investigated. [62]

2.4 Characterization of compatibilized blends

There are different aspects to characterize in compatibilized polymer blends: some of them focus more on the effect of compatibilization on the end properties of the material and not on the actual chemical products resulting in reactive blending. These types of characterization methods are morphological and mechanical methods. The structural characterization focuses on providing information of the actual chemical structures obtained in the blend. By combining these methods a wide range of information may be gathered, for example on the compatibilization efficiency, homogeneity of the blend and the effects of blend composition. The methods based on the end-property characterization are thought to be simpler as the concentrations of functional groups and thus the concentration of formed compatibilizer are rather low and thus the sensitivity of structural characterization methods has to be sufficiently high. This section covers the most common characterization methods by dividing them into morphological, mechanical, structural and other characterization methods.

2.4.1 Morphological characterization

The aim for the morphological characterization is to define the phase structure, that is, for example the size and distribution of the dispersed phase droplets and the texture and homogeneity of the polymer blend in general. Morphological characterization can also study the character of interfacial layer and identify the existence of micelles, or mesophases. [5]

One of the most often used method for morphological characterization is to use scanning electron microscopy, SEM. It gives visual images of the material surface based on the behaviour of the electron beam as it hits the surface. From the produced images the particle size and shape of the dispersed phase, for example, can be determined. Also the evolution of the structure based on processing conditions can be studied by using SEM. Transmission electron microscopy, TEM, is more time-consuming method, but in addition to the morphology description similar to SEM, TEM provides a wider scale of possibilities, such as localisation of a block copolymer used as a compatibilizer in blends of immiscible polymers. [5]

Figure 2.11 presents an example of the differences in SEM micrographs obtained at the surfaces of fractured samples of PE/PA blends with and without compatibilizer. Figure 2.11a represents a blend with composition of PE/PA 80/20 and Figure 2.11b represents a blend of PE/PA/PE-g-OXA 75/15/10, where PE-g-OXA is the oxazoline grafted polyethylene acting as a compatibilizing precursor in the blend. It can be seen in the figures how the particle size degreases significantly after the addition of compatibilizer and the structure is altogether more uniform. [28]

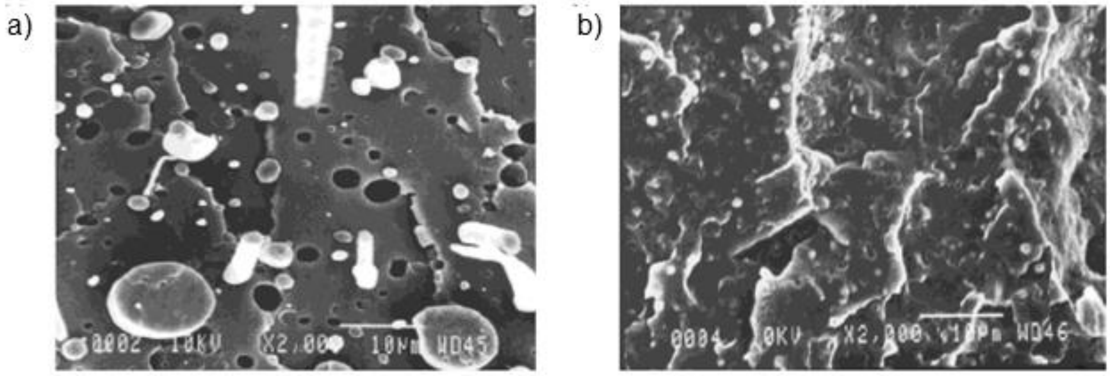


Figure 2.11 SEM micrographs of fracture surfaces of a) uncompatibilized and b) PE-g-OXA compatibilized samples [28]

Light scattering methods can study larger blend volume than electron microscopy methods and it has been used to detect phase transitions in polymer blends and in determination of droplet size, not only in the solid but also in the molten stage. [5]

Also other methods can be deployed when determining the morphology of polymer blends. Wide-angle X-ray scattering, WAXS or small-angle scattering, SAXS methods can be used to study the crystallisation in blends of semicrystalline polymers [5]. Ultrasonics have also been used to characterise morphology and it has been even used in situations where rapid, in situ characterization for melt blends has been needed [29].

Differential scanning calorimetry, DSC, can be used for discrimination between miscible and immiscible blends. As the technique measures the changes in enthalpy of the studied material under a certain temperature-time program it is possible to couple the thermal behaviour with diverse physical and chemical events. DSC technique enables the evaluation of heat absorbed or emitted and thus information on, for example, glass transition, melting and crystallisation can be obtained. [74] The presence of only one glass transition temperatures, T_g, is an indication of a miscible blend and two T_gs indicate an immiscible blend [50]. For partially miscible systems two T_gs shifted to the direction of their average can be obtained [5].

2.4.2 Characterization of mechanical properties

In many cases, mechanical properties can be used as an indicator of the compatibilization efficiency as the formation of inter-chain copolymers generates a stress transfer mechanism between the two immiscible phases and enhances the interfacial adhesion. Properties, such as tensile strength, impact strength and tensile modulus have been used to screen the changes in the stress transfer abilities and thus, the compatibilization efficiency. [5]

Hamid et. al. [15] reported on the studies on the mechanical properties of PA6/HDPE-g-MAH/HDPE blends. They studied a series combination of PA6/HDPE (70/30) blends with varying amount of compatibilizer. Their studies showed an increase in many mechanical properties, such as tensile modulus, tensile strength, flexural modulus and hardness when incorporating up to 2 wt.% of compatibilizer into the blend structure. This amount was enough to increase the interfacial adhesion between the blend components as the HDPE-g-PA6 copolymer was formed during reactive blending. With excess amount of compatibilizer (over 2wt.%) these properties started to gradually decrease.

2.4.3 Structural characterization

Structural characterization gives more detailed information about the chemical structure of the blend, that is, the structure of the blend components, and about the bonds formed during reactive processing.

The simplest aim for the structural characterization is to provide some evidence on graft-copolymer formation. For blends of PE and PA this type of characterization method is the Molau test [75]. It is a qualitative method for assessing the compatibilization efficiency as it detects the formation of PE-g-PA compatibilizer. The test can be used to prove, that the reaction between polyamide and compatibilizer precursor, such as HDPE-g-MA, actually happens. The method is related to fractionated dissolution as the compatibilized blend sample is diluted in formic acid and the graft or block copolymer formed during blending can then act as an surfactant and stabilize the colloidal suspension of polyolefin particles into the formic acid suspension. The formation of a stable suspension can be taken as an indication of the presence of PE-g-PA copolymer. [16; 27; 75]

Another method to indicate the presence of the compatibilizing graft copolymers is Fourier transform infrared, FTIR spectrometry. FTIR, or more commonly known as infrared, IR spectroscopy can be used to identify polymeric materials as the method is able to identify all the characteristic molecular rotations and vibrations induced by the electromagnetic radiation in IR region. As a result the IR absorption pattern for every material is unique and it correlates to the molecular structure of the material, and therefore, the formed bonds and functionalities can identified. [74]

In addition to the determination of miscibility of polymer blend, DSC traces can also be used in characterization of the interactions between the blend phases and, thus, to get some information on the structure. An example of changes in DSC traces depending on the type and amount of the compatibilizer and the structures in the blend, reported by Anttila et al. [76], is represented in Figure 2.12. In the melting thermographs of uncompatibilized (B 0) and compatibilized (B 10-15) PE/PA blends it can be seen how the melting peaks of PA (around 220 °C) and PE (around 115 °C) shift towards each other as compatibilizer is added in the blend. Also the melting peak representing PE becomes wider. The widening is suggested to be due to the different crystallisation temperature of PE phase and the compatibilizer. [76]

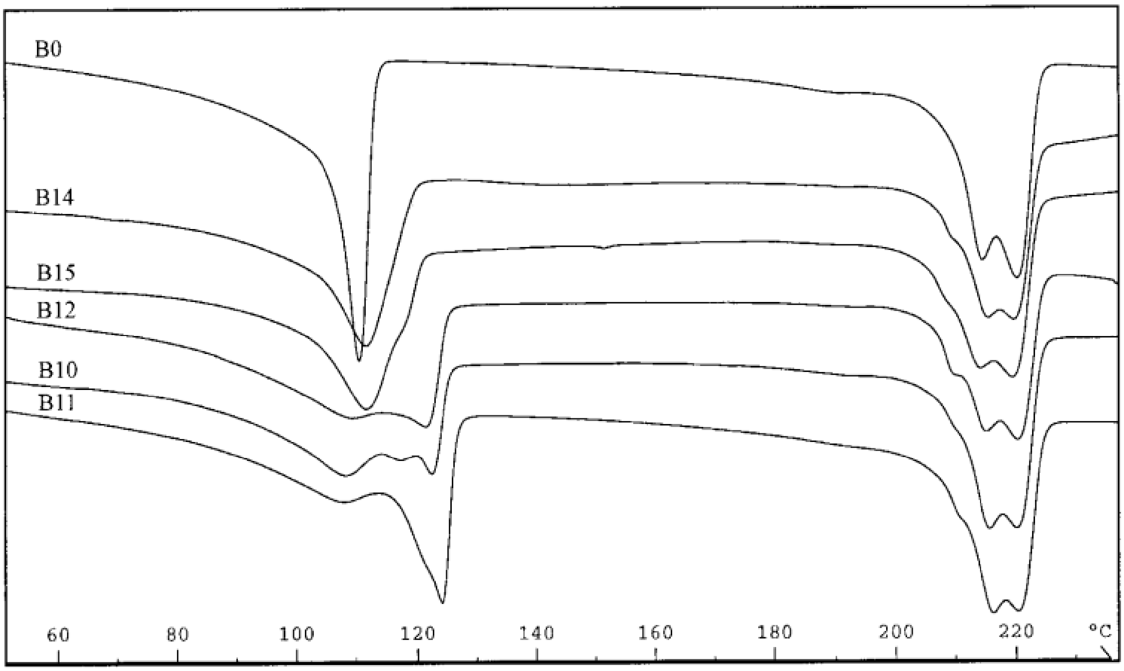


Figure 2.12 DSC melting curves of uncompatibilized and compatibilized PA/PE blends. [76]

DSC can also be deployed in obtaining fractionated crystallisation in immiscible polymer blends and the evolution of this phenomenon can be used as an indicator of the compatibilization efficiency. The fractionated crystallisation is based on the different type of crystallization processes (homogeneous, heterogeneous and self-nucleation) in polymer melts, as the bulk polymer is subdivided into isolated regions, such as droplets of the minor phase dispersed into immiscible polymer matrix. The crystallization upon cooling from the melt can occur in several temperature intervals that are initiated at different undercooling due to the finer particle size of the droplets. In these cases the crystallization may end up occurring at the homogeneous crystallization temperature, $T_{c,hom}$. Compatibilization of immiscible blends has been observed to affect the crystallization behaviour mainly by affecting the size and number of the dispersed phase droplets but it has also been suggested that it is partially due to the isolating core-shell structure that the compatibilizer forms around the droplets preventing the direct nucleating effect from one phase to another. It has also been shown that fractionated crystallization is related to the lack of active nuclei in the dispersed droplets by means of self-seeding experiments by Sánches et al. [77]. The evolution of the delayed crystallization peaks, that is, the shifting of the peaks towards lower temperatures, in DSC scans of compatibilized immiscible polymer blend can thus be used in qualitative evaluation of the compatibilization efficiency of the studied polymer blend. The stronger the shift of the peak is the higher compatibilization efficiency the blend has. [32; 78; 79]

Pang et al. [80] were able to link the glass transition process and the degree of compatibilization. They studied the thermal properties of PE/PA blends and found that the heat capacity increment at the glass transition (ΔCp) is a sensitive and important parameter for quantitative characterization of the degree of compatibilization. This is because the change of ΔCp is actually a measure of interfacial content. Thus, the magnitude of ΔCp value provides a quantitative measure of the degree of compatibilization.

2.4.4 Other characterization methods

The rheology of a polymer blend is an important factor when concerning the process ability of the material. The melt state behaviour has also been shown to relate to other blend properties and morphology and therefore, rheological characterization is also an informative characterization method.

Kudva et. al. [19] studied the rheological properties of a binary blend of PA6/PE-g-MA by using torque rheometer. Torque rheometers are usually a part of a normal mixer or extruder and it is essentially an instrument that measures viscosity-related torque caused by the resistance of the material to the shearing action of the plasticating process [81]. The Brabender torque of blends of PA with various maleated polyethylenes were measured and their results are shown in Figure 2.13.

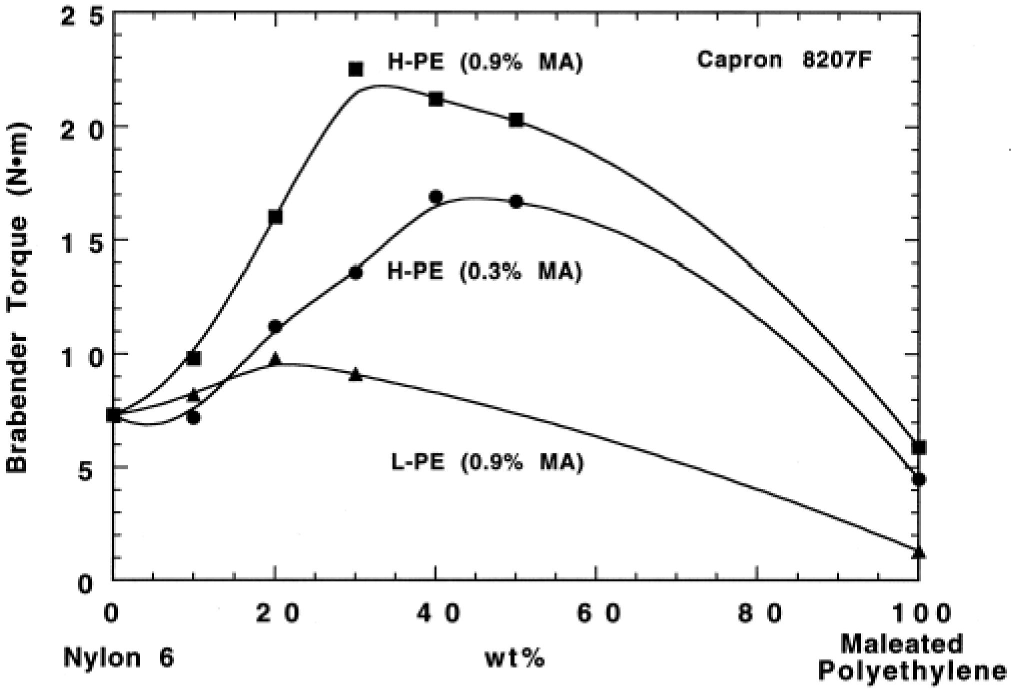


Figure 2.13 Effect of blend composition and the type of compatibilizer precursor on the rheological properties. [19]

As presented in the graph, each of the blends has a higher Brabender torque than either of the blend components which is evidence that grafting reactions occurred. Higher MA-content leads to a higher torque and with same MA content the PE with higher viscosity reveals a substantially higher torque. A somewhat larger torque was expected based on the physical consideration of mixture additivity of viscosity, but in addition it was also speculated that the extent of grafting is greater when two pure phases become nearly matched in melt viscosity since this will tend, just on physical grounds, to lead to a finer dispersion or more surface area where grafting can occur. [19]

Melt flow rate (MFR) can be used to measure the melt flow of a polymer melt trough a die at a certain temperature under a certain weight [74]. The test is normally used in quality control and it is an indirect measure of molecular weight and it is inversely proportional to the viscosity of the melt under similar conditions. Low MFR is an indication of high molecular weight and vice versa.

Other methods deployed in characterization of polymer blends are for example Dynamic Mechanical Analysis, DMA [14], Thermogravimetric methods (TGA) [27] and three point bending test of shape memory experiments [21].

3. BLENDS OF POLYETHYLENE AND POLYAMIDE

Polyethylene and polyamide form an immiscible blend due to the differences in the polarity. The blend has been under extensive studies during the past two decades due to the versatility of the properties of the blend when compatibilized properly. Polyethylene offers sealability, processability, flexibility, impact strength and moisture insensitivity, whereas polyamide offers strength, thermal stability and barrier properties. By blending new property combinations may be reached. [6; 16]

This chapter is a case study of the blends of polyethylene and polyamide. The first sections cover the basics of polyethylenes and polyamides, and the next sections of the chapter focuses on different blend components and compatibilization methods used in PE/PA blends. The last section covers more thoroughly the use of maleic anhydride as the coupling agent in these blends and the effect of the blend composition on the properties of the final blend.

3.1 Polyethylene

In general polyethylenes are semi-crystalline thermoplastic polymers with a range of mechanical properties depending on the material density, and for example the high density PE is the most rigid and the low-density PE more flexible. It has good moisture resistance and it chemically inert with a range of substances. [82; 83]

Low-density polyethylene, LDPE was the first thermoplastic polyolefin used commercially. It is also known as “high pressure” polyethylene because it is exclusively made by high pressure process. The structure of LDPE is branched, as represented in Figure 3.1 due to the free radical polymerization. The branching of LDPE gives it a unique rheological behaviour and properties and it is used widely in film, coating, wire and cable, and moulding applications. The properties of LDPE are dependent on the structure of the polymer chains, i.e. the molecular weight, molecular weight distribution, MWD, frequency of short-chain branches, and frequency and length of the long chain branches. [83]

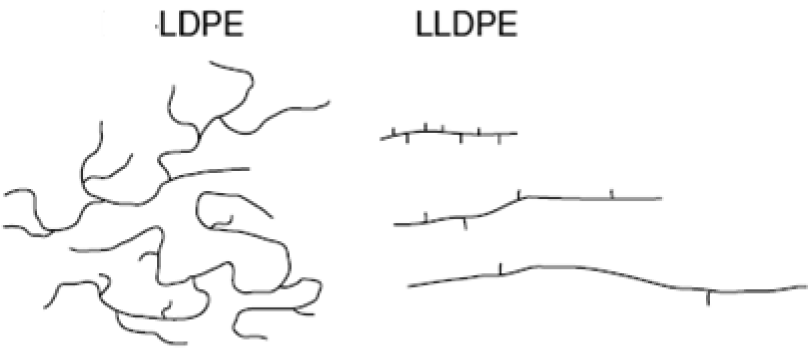


Figure 3.1 Structural differences between high-pressure LDPE and conventional LLDPE. Adapted from: [84]

High density polyethylene, HDPE, is a predominantly a linear polymer with some short chain branching. As the name says, the density of HDPE is high, ranging from 0.941 to 0.961 g/cm^3 or even over that. HDPE is polymerized by low-pressure process using catalysts, such as the Phillips chromium catalyst, Ziegler-Natta catalyst or metallocene catalyst. [59, 82]

The structure of *linear low-density-polyethylene, LLDPE* resemble more of HDPE as it lacks the long-chain branching of LDPE. Also the molecular weight distribution of LLDPE is narrower than that of LDPE. The polymerization process is similar to the low-pressure processes of HDPE and the density of LLDPE is strongly controlled by comonomer (such as hexene, butene or octene) content and distribution. Most of the branching due to comonomer is randomly distributed along the polymer backbone. [84]

It has been stated that the properties of polyethylenes depend on the structure of polymer chain, especially on molecular weight and molecular weight distribution. Generally, the high MW results usually in better mechanical properties of the final product, but the high MW will also bring rise to high melt viscosity and poor processability. On the other hand, with low-molecular weight the properties go vice versa. This conflict between processability and mechanical properties has been recently resolved by using polyethylene with bimodal molecular weight distribution, defined as bimodal PE. [85]

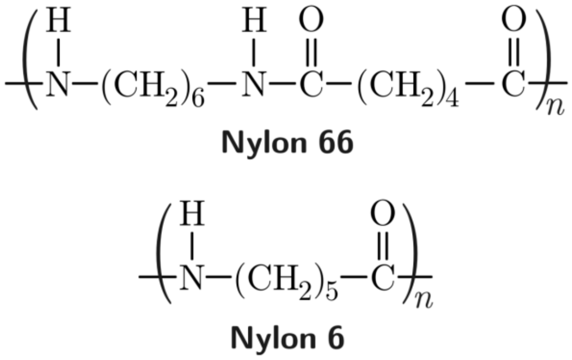
The *bimodal PE* is composed of low molecular weight PE fraction responsible for stiffness and creep resistance in crystalline phase and the lower melt viscosity during processing, and of high-molecular weight fraction, which acts as the tie molecule connecting the crystalline lamellae and therefore improves the impact strength and stress cracking resistance. [85]

3.2 Polyamide

Polyamides are a family of materials containing different monomers combined by amide (–NH-CO-) bonds. The type of polyamine depends on the monomers employed.

Polyamides are also called as ‘nylons’ in the terminology when referring to aliphatic and semi-aromatic polyamides, and ‘aramides’ when referring to aromatic polyamides. [86]

The most important polyamides are nylon 6 and nylon 66 (Figure 3.2) accounting for more than 90% of polyamide usage. The number in the type of polyamide corresponds to the number of carbon atoms in the monomers, that is, the nylon 6 consists of one monomer, lactam, that includes both amine (-NH_2) and acid (-COOH) functionalities and nylon 66 consists of dicarboxylic acid and diamine monomers. [86; 87]



$$\left(\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\right)_n$$

Nylon 66

$$\left(\overset{\overset{H}{|}}{N}-(CH_2)_5-\overset{\overset{O}{\|}}{C}\right)_n$$

Nylon 6

Figure 3.2 Polyamide 6 and polyamide 66 structures [88]

Polyamides are engineering thermoplastics with a combination of mechanical and thermal properties that allow them to be employed for highly specified end uses. Polyamides are used in fibrous form to reinforce composite structures and as main material for example in textiles and automotive applications. In packaging applications polyamides are used for example in multilayer film to bring mechanical strength and barrier properties. [87]

3.3 Compatibilization of PE/PA blends

The most common methods to compatibilize PE/PA blends are the addition of reactive polymer, the in situ functionalization and addition of low-molecular weight reagents. As noted before, there are several functional groups capable to react with the amide and acid functionalities of polyamide. Not only polyethylene is used as the backbone for the reactive polymer but also other polymers miscible with polyethylene are used, such as styrene ethylene butylene styrene copolymer, SEBS; or ethylene propylene diene rubber, EPDM.

The blend of polyethylene and polyamide has many potential compositions as there are different types of polyethylenes and polyamides from which to choose. Burgstaller et al. [9] studied the influence of polyethylene type, that is, HDPE, LDPE and LLDPE, on the properties and morphology in PE/PA blends. They had two approaches to generate the compatibilizer in situ: the use of prefabricated PE-g-MA compatibilizer precursor and forming the compatibilizer in situ by grafting the MAH molecules onto the PE chain and forming PE-g-PA graft copolymer compatibilizer in a single step. They compared the mechanical, rheological and morphological properties of three different PE/PA blends containing HDPE, LDPE and LLDPE, respectively. All the blends with different types of PE showed significant effects on the properties and morphology when compatibilized, such as reduction in domain size of the dispersed phase and increased impact strength. The differences between the polyethylene types were only minor and it was suggested that these small differences were due to the different viscosities and the resulting shear forces in the blends. [9]

In studied of Kudva et al. [19] the effect of melt viscosity on the properties was studied. As blends of high viscosity PA6 and different maleated polyethylenes were studied the low viscosity maleated polyethylene was found to be ineffective for toughening two nylon 6 materials with different MW and different viscosities. This was suggested to result from the large mismatch in the melt viscosity of the blend components because the low viscosity PE phase tended to become continuous even when it was the minority component. The blend was suggested to be near the phase inversion point which is for non-reactive systems given by the following equation:

$$\frac{\eta_1\phi_2}{\eta_2\phi_1} = 1, \tag{2}$$

where the η_i is the melt viscosity of the phase *i* and ϕ_i is the volume fraction of the phase *i*. The differing viscosities were also found to affect the grafting yield as the larger mismatch between the blend components resulted in lower torques during blending and thus, less formation of PE-g-PA compatibilizer, than with the blend with viscosities closer to each other. The toughening abilities of the high viscosity polyethylenes, both, with 0.3 and 0.9 wt.% of anhydride contents were found to be significantly better for high viscosity PA.

Most studies on PE/PA focus on blending PA6 of all the polyamide types. This is most probably due to the simplicity of the structure and the general usage in the industry for extrusion and injection moulding, whereas nylon 66 is more used in fibrous applications. [89]

The selection of a suitable compatibilizer precursor is one of the most critical factors in compatibilization process and the selection from which to choose is wide. The most frequently used are MA-functionalised polyethylenes [4; 7; 9; 11; 15-18; 21] and ethylene glycydyl methacrylate copolymer, EGMA [10; 22; 30; 32]. Other polyethylene based reactive polymers are, for example, ethylene oxide (PEO) [14], ethylene acrylic acid, EAA [22; 32; 34; 90], silane grafted polyethylene, HDPE-g-Si [25], isocyanate grafted polyethylene, HDPE-g-HI [23], oxazoline grafted PE [28; 91], and polyethylene functionalized by using metallocene catalysts, NHMe, and resulting in functional groups of -OH, COOH, [76]. The utilization of a third component in the blend is also a common method, as long as the third component is miscible or at least partially miscible with one of the two main phases, usually with polyethylene. Examples of these type of compatibilizer precursors are such as MA or GMA grafted styrene ethylene butylene styrene, SEBS [11; 12], MA-grafted styrene ethylene propylene copolymer, SEP-g-MA [11], ethylene vinyl acetate, EVA, and ethylene butyl acrylate copolymer EBA, both with MA functionalities [8], and maleated ethylene-propylene diene rubber EPDM-g-MA [20; 26].

A different approach for compatibilization of blends of polyethylene and polyamide was taken by Araújo et al. [4] and Vallim et al. [27] who used recycled, post-consumer HDPE, rHDPE, as a compatibilizer. The rHDPE possesses polar groups formed by oxidative degradation during its use and disposal and these polar groups are able to form chemical bonds between PE and the amine groups of PA. It was shown, that the rHDPE improved the mechanical properties of the blends more than the use of PE-g-MA as a compatibilizer precursor. Also the domain size of the dispersed phase droplets was reduced in the same magnitude as when using PE-g-MA.

The use of recycled blend components does not limit only to compatibilizer, but recycled polyethylenes and polyamides have been studied by several researchers. Recycled polyethylenes and polyamides have been studied when blended with other polymers [92; 93] and with each other [4; 27; 94]. Blends of post-production LDPE with a small amount of polyethylene methacrylic acid, EMAA, and post-consumer PA 66 were studied by Desiderá and Felisberti [94].

Also multilayer polymer waste containing among others PE and PA has been an interest of study. Hong et al. [95] studied blends of polypropylene and post-consumer nylon waste (containing also LDPE and LLDPE) and the addition of compatibilizers was shown to improve the mechanical and rheological properties, reduce the domain size and refine the coarsening of the morphology. In the studies of Choudhury et al. [96] a post-consumer waste oil pouch made of co-extruded multilayer film was under inspections. Pouches were reported to contain about 83 wt.% of LDPE/LLDPE mixture, 15 wt.% of PA and 2 wt.% of additives. The use of compatibilizer was found to improve remarkably the interfacial adhesion between PE and PA phases and therefore also the mechanical properties and thermal stability.

The comparison between the reactive polymers is not straight forward but some studies have also been reported on that matter. Many studies focus on comparing different compatibilizers to each other e.g. in the field of compatibilization effectiveness or reactivity. The research group of Filippi et al. [10-12; 16; 34] studied the effect of compatibilizer precursors on morphology and mechanical properties of PE/PA blends. They discussed about the effectiveness of different type of compatibilizers, i.e. ethylene acrylic acid copolymers, EAA, [34; 90], maleic anhydride grafted polyethylenes, PE-g-MA

[16], ethylene glycidyl methacrylate copolymers, EGMA [10], styrene ethylene/butylene styrene copolymers, SEBS grafted with MA and GMA [12] and MA-grafted styrene ethylene/propylene copolymer SEP-g-MA [11]. The results of their studies confirmed that the compatibilizers with MA-functionality are more effective compatibilizers for LDPE/PA blends, than that of the ethylene-acrylic acid and ethylene-glycidyl methacrylate copolymers. The efficiency of different MA grafted compatibilizer precursors was shown to depend on the structure and molar mass of the back bone chain. The effect of the type of polyethylene is discussed further in the section 3.4.2 but in general the PE-g-MA showed a slightly lower activity than SEP-g-MA or SEBS-g-MA towards 75/25 LDPE/PA blends. However, all the studied maleated CP's demonstrated to be effective when used to compatibilize blends of polyethylene and polyamide [11].

The type of compatibilizer has been shown to affect the crystallization behaviour of compatibilized immiscible polymer blends. The effectiveness of three different compatibilizers studied by Filippi et al. [10-12; 16; 34] was rated qualitatively by Yordanov and Minkova [32] who studied fractionated crystallization phenomenon and polydispersity of the dispersed PA phase in compatibilized 75/25 PE/PA blends. They observed clear fractionation in the crystallization with two of the studied compatibilizer precursors and by the extent of the fractionated crystallization they were able to suggest a qualitative evaluation of the degree of compatibilization. The studied CPs were rated according to their reactivity as follows: SEBS-g-MA > EAA > EGMA.

3.4 Maleic anhydride as coupling agent in PE/PA blends

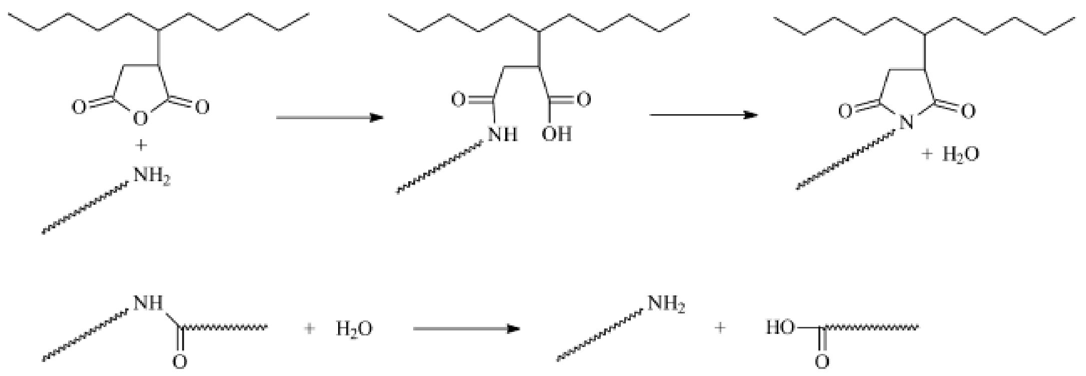
Using maleic anhydride grafted polyethylene as the compatibilizing precursor seems to be the most deployed method when compatibilizing the blends of PE and PA. This section focuses on blends in which MAH acts as a coupling agent, mostly while grafted on PE chain. The first sub-section covers the compatibilization reaction between PA and MAH, and the factors affecting this reaction. The second sub-section focuses on the effects of the blend composition variation in PE/PA/CP blends on the properties of the final material.

3.4.1 Compatibilization reaction between PA and MAH

Polyamide usually contains the reactive groups of amine and/or carbocylic acid. Polyamide 6 and polyamide 66 most often contain both of the functionalities due to the ring opening polymerisation of PA 6 or by polycondensation of PA 66. Therefore, the reactive polymer has 3 different potential functionalities to react with: amine (-NH2) and acid (-COOH) end groups and in-chain amide (-NH-CO-) groups. It has been shown that the compatibilization reaction between PA and MAH results in generation of amide or imide linkage. [97]

The amide and imide linkages may form in two ways between MAH and PA: the anhydride group reacting either with the amine end group of PA or with the in-chain amide groups. These two reactions are illustrated in Figure 3.3. The reaction between MAH and amine end-groups is a condensation reaction consisting of two steps: the reaction of anhydride group with one amide forms an amic acid function, which then transforms into an imide cycle generating one water molecule. The formation of water molecule may lead at certain processing conditions to hydrolysis of PA and, thus, the two reactions may lead to same reaction products. The hydrolysis may be prevented by proper ventilation of the extruder. [7; 16]

a) reaction with the amine end groups of PA:



b) reaction with the in-chain amide groups of PA:

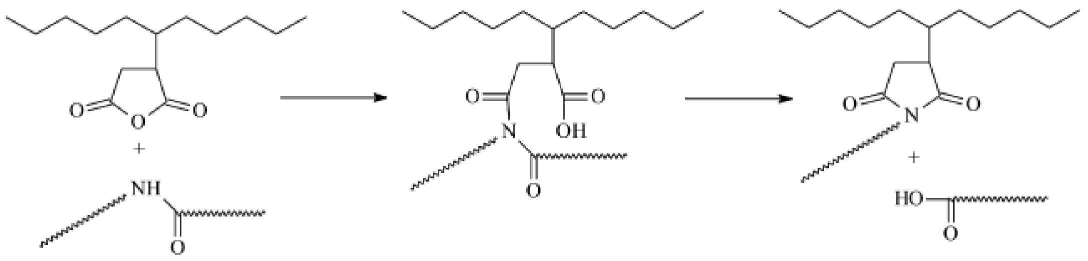


Figure 3.3 Schematic presentation of maleated polyethylene reacting with a) the end b) the in-chain groups of PA [16]

Maréchal et al. [98] compared the reactivity and reaction kinetics of amine end groups and in-chain amide groups when reacting with succinic anhydride group. Their studies showed that the mechanism in which the anhydride reacts with the amine chain end group is dominant in the early stages when the starting amine concentration is high. Even though the amide concentration in polyamide is much higher than the amine concentrations, the amine-anhydride reaction is much faster and, thus, when the anhydride concentration is lower than the amine concentrations, the amide-anhydride reaction is negligible. The concentration of the amine chain ends will increase via hydrolysis usually only in the case when there are more anhydride groups than amine groups as the reaction kinetics of the hydrolysis is quick enough. [98]

The conversion rate of the reaction between amine and anhydride groups is affected by many factors, such as processing condition, the structure of the CP and the blend composition. The reaction kinetics was found to be affected by the monomer structure on amine-anhydride reactions at polymer/polymer interfaces. Jones et al. [99] studied the variation in thermodynamic interaction parameter χ by changing the chemical structure of the backbone. It was shown that both increased χ and molecular weight decrease the conversion rate and degree.

The conversion ratio was studied by Argoud et al. [7] by mixing 60 vol. % of PA 6 with a mixture of HDPE and HDPE-g-MA in which the fraction of the CP decreased from 40 vol.% to 0. The conversion degree was obtained from the absorption band of anhydride carbonyl in the IR spectra which indicated the unreacted anhydride moieties. The obtained conversion rates were plotted as a function of the initial molar ratio of MA groups on amine end-groups and these results are presented with black diamond symbols in Figure 3.4. The maximum theoretical conversion rate is also presented with continuous line in the same graph.

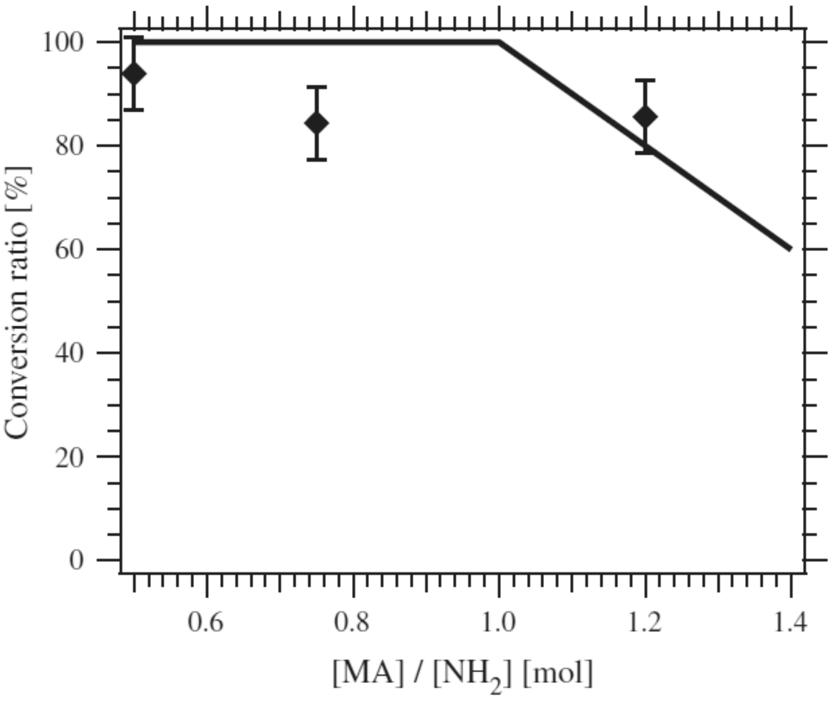


Figure 3.4 Maximum theoretical (continuous line) and experimental (diamond symbols) conversion rates versus the initial molar ratio [MA]/[NH$_2$] studied by Argoud et al. [7]

Argound et al. presented an example of a blend with composition of PA/PE/CP 50/30/20 vol.% with a ratio [MA]/[NH_2]≈1, for an estimated conversion ratio of about 80%, as in Figure 3.4, 80% of PA chains are grafted to PE-g-MA, while 32 vol.% of PE phase (80% of the 40 vol.% of the compatibilizer precursor on PE phase) is constituted of the PE blocks of the graft copolymer. The result is that the graft copolymer is the majority component in the material. [7]

3.4.2 Effects of the blend composition

It has been many times already demonstrated how the variations in the blend composition of PE/PA/CP blends have an effect on the morphology and the final properties of the blend. The estimation of these effects is not always simple as the blend has 3 components and the changes in the concentration of one component changes the relative proportions of the other component also, and thus, tertiary blends are complex systems. No simple binary graphs can be drawn, unless one, or even two, of the components are kept constant.

The ratio of polyethylene and polyamide is a rather dominant factor affecting the properties of compatibilized PE/PA blends. In studies by Araújo et al. [4] the maximum yield stress of injection moulded test specimens with different blend compositions were compared. They studied the uncompatibilized and compatibilized (by 2 wt.% of PE-g-MA) HDPE and recycled post-consumer polyethylene, PEpc in blends with PA6 over the whole range of composition from 0 to 100 wt.% of PA6. As shown in Figure 3.5 the trend set by the uncompatibilized blend is repeated by the compatibilized and recycled blends, though, the results of the compatibilized blends are significantly higher values than those of the uncompatibilized blend. The trend is set by the continuous matrix phase.

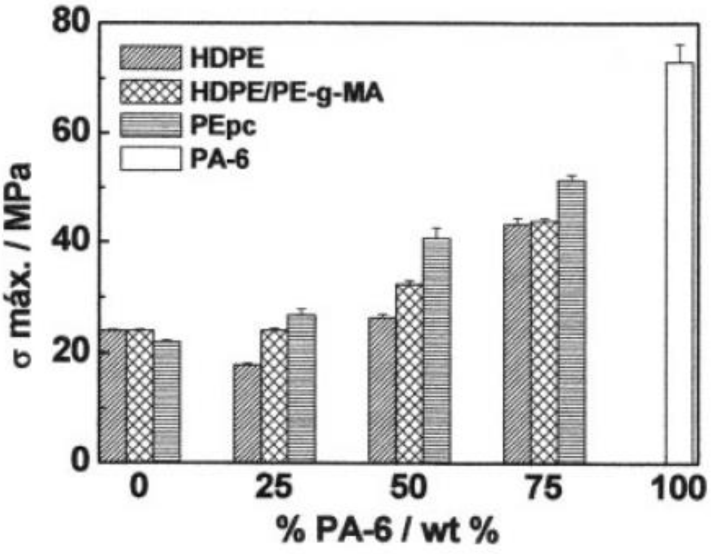


Figure 3.5 Variation of the maximum yielding stress, σ_{max}, as a function of composition for PE/PA blend with different compatibilizers. [4]

The morphologies of tertiary HDPE/PA6/CP blends over a wide range of compositions prepared by reactive extrusion were studied by Argoud et al. [7]. They focused especially on high concentrations of the compatibilizer precursor and used SEM images to analyse the morphology with varying compositions. They observed 5 different morphologies: 1) PA droplets dispersed in a PE phase matrix; 2) PA stretched dispersion in a PE phase matrix; 3) co-continuous (the situation in which both phases form single co-continuous domains, without isolated drops); 4) PE phase stretched dispersion in a PA matrix; 5) PE phase droplets dispersed in a PA matrix. [7]

There are two ways to alter the MA content in a blend: by varying the grafting degree or the reactive polymer or by altering the concentration of the reactive polymer. Same total concentrations of MA moieties can be obtained by both methods, but as denoted earlier, the structural characters, such as grafting degree, can affect the reactivity of the compatibilizer precursor, and therefore the effect of grafting degree and concentration of compatibilizer precursors are elaborated here separately.

Commercially the content of MA grafted on the polyethylene is usually between 0.5 and 2 wt.% [57]. *The effect of grafting degree* was studied by Jiang et al. [16]. They compared the evolution of particle size and torque at the end of mixing as a function of MA grafting level in the compatibilizer precursor when keeping the PE/PA/CP ratio as constant. Their studies supported the findings of Kudva et al. [19], who reported of increasing torque as the MA content increased from 0.3 to 0.9 wt.%, as reported in the context of characterizing the melt viscosity properties of polymer blends in section 2.4.4. The results of Jiang et al. indicated that a strong enhancement of dispersion of PA droplets is found by using a CP with only 0.3 wt.% of MA, and that no further improvement is obtained by increasing grafting degree beyond 0.8 wt.%. This effect was paralleled by an increase of melt viscosity, indicated by the final torque at the end of mixing which also sets on a plateau after 0.8 wt.% of MA. [16]

Chuai et al. [70] reported on an apparent increase in tensile strength with increasing grafting degree of MAH onto PE chains. The grafting degree was determined by using FTIR characterization. The authors studied 70/30 LDPE-g-MA/PA6 blends and according to their results the tensile strength increases up to 5.1% of grafting degree and above that it starts to decrease. This observation is also supported by Kudva et al. [19] who reported on increase in the mechanical properties by increasing MA grafting degree.

The effect of the amount of compatibilizer precursor was studied by Jiang et al. [16]. While altering the amount of CP the ratio of polyethylene and polyamide was kept constant. They evaluated the effect on the particle size distribution of the dispersed phase and the final torque while preparing the blends. The studies showed quite clearly that the average dimension of the dispersed PA droplets decrease appreciably with an increase of the CP concentration, and the size distribution becomes considerably narrower. The distribution curves for a 75/25 PE/PA blends with varying CP concentration are presented in Figure 3.6.

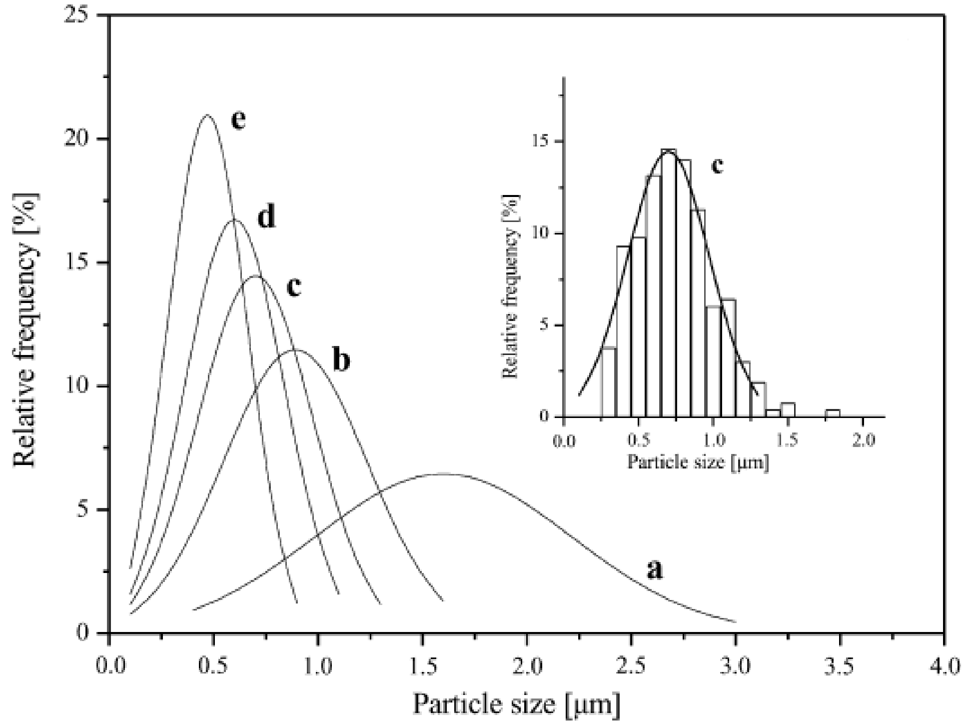


Figure 3.6 Particle size distribution for the 75/25/x PE/PA/CP blends a) x=0, b) x=3, c) x=5 d) x=8, and e) x=10 wt.% [16]

The five morphology classes obtained by Argoud et al. [7] were shown not to depend strongly on the amount of reactive polymer, but the volume ratio PE/PA. By increasing the compatibilizer amount, the characteristic size becomes smaller. Compatibilizer also suppresses coalescence and stabilises the micrometre scale morphologies. Their major observation was that even in the systems which contain a large amount of compatibilizer, only a very small fraction of the formed copolymer is located at the well-defined interfaces of the larger scale (micrometre) morphologies.

Even though in the scales relevant to processing the PE-g-MA is considered to be miscible with neat PE, there are some indications denoted by Argoud et al. [7] that MA groups are not miscible with polyethylene at the molecular scale. These indications rely on the calculations that they performed related to the Flory-Huggins interaction parameter χ between PE monomer and MA groups which indicate that PE-g-MA should be considered as a copolymer containing entities not miscible with PE. For example, the results of the rheology measurements in their studies were thought to be a possible indication of the presence of micelles of MA moieties bridged by PE chains. However, the studies of Jiang et al. [16] demonstrated that total miscibility of compatibilizer with the matric phase is not always desired but the migration of the CP to the interface between PE and PA phases and thus the compatibilization reaction is more likely to occur.

4. RESEARCH MATERIALS AND METHODS

The experimental part of this thesis evaluates the behaviour of a bimodal LLDPE as a matrix material in blends with polyamides and recycled blends when compatibilized by using maleic anhydride grafted polyethylene. This chapter presents the materials, sample preparation and the research methods used in the experimental part.

4.1 Materials

A bimodal Borstar® LLDPE with the density ρ=0.926 g/cm^3, referred later as PE, was used as a basic matrix component in this study. The grade is typically used in packaging film applications. The product used as the compatibilizer precursor is a maleic anhydride grafted polyethylene, referred as compatibilizer precursor, CP. The density of the CP was ρ=0.934 g/cm^3 and the grafting degree about 0.5 wt.%. Both products were manufactured by Borealis Polymers and were in a form of pellets.

The polyamide grades used in this study were in a form of pellets. Two different polyamide 6 grades were used: a low viscosity PA and a medium viscosity PA, referred here as PA-L and PA-M, respectively. The density of both grades was ρ=1.13 g/cm^3.

The recycled product, referred as R or R100 when studied on its own, in this work was a blend of two different multilayer packaging films known to contain a layer of polyamide for oxygen barrier. Films were received from a film manufacturer in a form of about 40 cm wide film rolls.

The polyamide content of the recycled blend was determined by measuring the basis weight (mass per square meter) of both films and using this value to calculate the density of the films. The basis weight was measured by die-cutting 3 round samples with 100 cm^2 area and weighing them. The basis weight of the film was, hence, the hundredfold value of the average the three measured samples. The total density of a film was assumed to be a function of the weight fraction of PA, when assuming that the rest of the film consists of materials with the density of LDPE, ρ_{LDPE}=0.920 g/cm^3, according to the following function:

$$\rho_{PA} * x + \rho_{LDPE} * (1 - x) = \rho_{Recyclate}, \tag{3}$$

in which x is the weight fraction of PA. These calculation resulted in 27 and 50 wt.% for the two characterized films, respectively. As the blend was prepared in 1:1 weight ratio of the two films, the final PA content of the blend was, thus, 38.5 wt.%. Due to the inaccuracy of this characterization method a value of 40 wt.% has been used in the thesis as the value for the weight fraction of polyamide in the recycled blend.

Based on the layer thickness measured from the cross-sectional light microscope images of the films the content by weight of the adhesive tie layers between the polyamide and LDPE layers was also calculated. By assumption of the density of the adhesive to be equal to the LDPE layers the content was assumed to be approximately 14 wt.%.

4.2 Sample preparation

This section describes the preparations made for the recycled film material in order to convert the form of the material from two separate film rolls into pellets, the compounding process and the sample cutting methods used to prepare the specimens for the mechanical tests.

4.2.1 Preparation of the recycled material

The recycled material used in this study was produced by blending the two received film materials together in a weight ratio of 1:1. As the material was in a form of film the blending required some preparations prior to the blending. The films were pressed in about 200 g stacks under elevated temperature (180°C) into 4 mm thick sheets. The sheets were then grinded into small flakes and the different film materials were dry blended. The flake blend was then processed through a Werner & Pfleiderer ZSK30W extruder at the temperature of 240°C. The blend was extruded into strings which were subsequently pelletized for further compounding.

4.2.2 Compounding

A range of compounds were prepared by varying the blend compositions, that is, varying the matrix by altering the concentration of the compatibilizer precursor, altering the content of the dispersed phase and by varying the type of the dispersed phase. The names that are later used to refer to these specific compounds and the compositions of the compounds are listed in Table 4.1. As the ratio of CP to PA was found to be a significant factor in the compatibilization efficiency the CP/PA ratio was calculated for each blend which included both of these components. In these calculations the PA contents of the recycled material was assumed to be 40 wt.%.

Table 4.1 Compounded polymer blends and their compositions

	Compound	Components	Ratios	CP/PA
Neat polymers	PE	PE	100	
	PA-L	PA-L	100	
	PA-M	PA-M	100	
Matrix blends	PE-A	PE/CP	95/5	
	PE-B	PE/CP	90/10	
Experimental blends	PE-L15	PE / PA-L	85/15	
	PE-A-L5	PE-A / PA-L	95/5	0.95
	PE-A-L15	PE-A / PA-L	85/15	0.28
	PE-A-M5	PE-A / PA-M	95/5	0.95
	PE-A-M15	PE-A / PA-M	85/15	0.28
	PE-B-L5	PE-B / PA-L	95/5	1.9
	PE-B-L15	PE-B / PA-L	85/15	0.57
Recycled blends	R100	R	100	
	PE-R30	PE / R	70/30	
	PE-B-R10	PE-B / R	90/10	2.25*
	PE-B-R30	PE-B / R	70/30	0.58*
	PE-B-R50	PE-B / R	50/50	0.25*

*PA content calculated with the assumption of 40 wt.% of PA in the recycled blend

The actual compounds were prepared by using Werner & Pfleiderer, ZSK30W, co-rotating twin-screw extruder, with L/D=38, which is designed for reactive extrusion. Figure 4.1 presents the twin screws used in the compounding. The screw speed was kept at 150-200 rpm, the screw temperatures were 200-240°C and throughput at 7-9 kg/h. The specific processing parameters per each produced sample are presented in Appendix A.

Figure 4.1 Co-rotating intermeshing twin screw from reactive extruder

The compounds were processed by dry blending the blend components in a form of pellets and reactively compounding them by feeding in to the extruder via a hopper and extruding into strands. The strands were subsequently cooled in a water bath and cut into small pellets by strand pelletizer. A schematic presentation of the compounding and pelletizing process is presented in Figure 4.2.

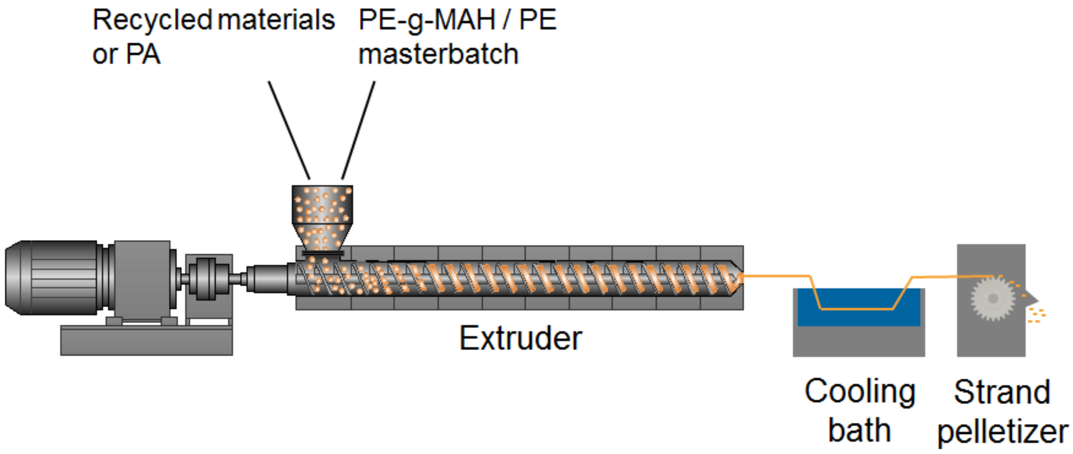


Figure 4.2 Compounding and pelletizing process

The matrix compounds were prepared by dry blending the neat polyethylene with 5 and 10 wt.% of maleic anhydride grafted compatibilizer precursor, CP and processing the blends through the extruder. After this, the matrix compounds were blended in different ratios with low viscosity polyamide, PA-L and medium viscosity polyamide, PA-M. The polyamide grades were dried for approximately 15 hours at 75 °C in order to remove the excess moisture as polyamide is a hydrophilic material and the excess moisture could cause volatilities during processing and cause hydrolysis in the PA chains. The compounds with PE and the recycled material were prepared in a same manner.

4.2.3 Sample pressing and cutting

The specimens for mechanical testing were prepared by compression moulding. The compounded pellets were pressed into 4 mm thick sheets by using two Teflon coated metal sheets and a rectangular mould under a specific compressing program presented in Figure 4.3. The maximum temperature during the program was 210 °C and the pressure applied was 5.0 bar.

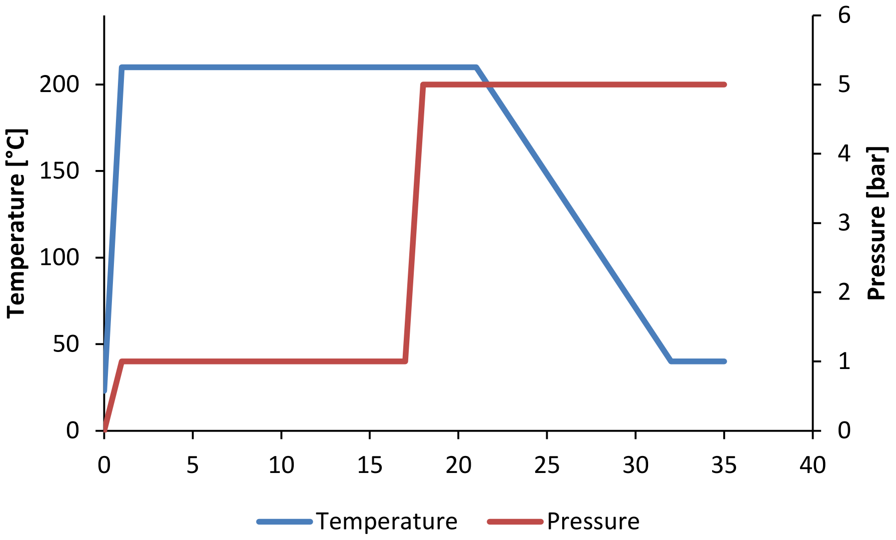


Figure 4.3 Compression moulding program

The dumbbell shaped test specimens for tensile tests were die cut from the sheets by using a specific die for the specimens defined in the standard ISO 527-1. The specimens for the Charpy impact tests were cut to the required dimensions according to the standard ISO 179-1 by using a circular saw.

4.2.4 Film manufacturing

Some of the produced compounds were converted into a form of film in order to analyse the homogeneity of the compounds. The converting was conducted by using Dr. Collin ESC T10 cast film extruder, which is presented in Figure 4.4. The compounds converted into film and the processing parameters that were used are presented in Table 4.2.

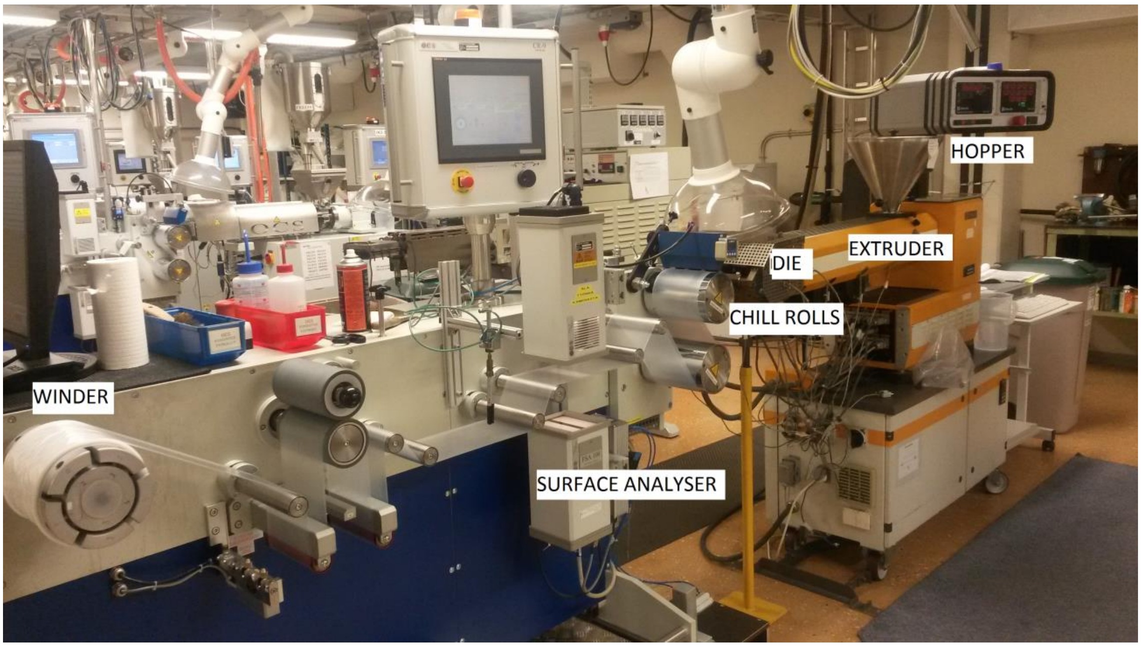


Figure 4.4 Cast film extrusion equipment

Table 4.2 Processing parameters

	Screw speed [rpm]	**Screw Temp. Profile [°C]**	**Yield [kg/h]**	**Film Thickness [μm]**
PE	23	175-240	1.8	41.8
PE-L15	34	175-270	3.5	476
PE-A-L15	31	175-270	2.8	170.9
PE-A-M15	31	175-270	1.9	166.7
PE-B-L15	31	175-270	2.8	93.4
PE-R30	31	175-270	2.6	67.6
PE-B-R30	31	175-270	1.7	121.7

Prior to the processing the granules were dried in a Heraeus vacuum oven at 80 °C for at least 45 minutes. The compounds were then fed into the hopper and extruded through an about 18 cm wide die on a cast chill roll (at temperatures 70 or 75 °C, depending on the compound). As the goal was to produce uniform film without holes and other defects some of the processing parameters had to be adjusted slightly depending on the compounds so that the converting was successful. Important factors were the temperature and speed of the chill rolls and the use of air knife after the die. Due to the small batch sizes of the studied compounds the optimization of the film conversion process was not possible and thus the same film thickness for all film samples was not reached.

4.3 Test methods

This section presents the test methods used to characterize the produced compounds. Impact and tensile tests are mechanical tests which give indications of the adhesion between the matrix and the dispersed phase. Optical microscopy and SEM analysis were conducted for the evaluation of the compound morphology. Melt flow rate and DSC give indications of the structures of the compound components.

4.3.1 Impact test

The Charpy impact strength of the produced compounds was measured according the ISO standard ISO 179-1 Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test. The standard specifies a method for determining the Charpy impact strength of plastics under defined conditions. The method can be used to investigate the behaviour of specified types of specimen under the impact conditions defined and for estimating the brittleness or toughness of specimens within the limitations inherent in the test conditions. [100]

Prior to testing the specimens machined from the compress moulded sheets into ISO 179-1/1eA specimens, with the dimensions of: length l = 80 ± 2 mm, width, b = 10.0 ± 0.2 mm and thickness, h = 4.0 ± 0.2 mm. The type A notch with depth of 2 ± 0.2 mm and the notch tip radius of r_N = 0.25 ± 0.05 mm was machined on the edge of the specimen. The specimens were conditioned in the standard atmosphere (23 ± 2 °C and 50 ± 5 % of relative humidity) for at least 16 hours prior to testing.

The tests were also conducted in the standard atmosphere by using Zwick pendulum-type testing machine and a 4.0 kJ hammer. At least 10 specimens were tested per sample. After the impact the break types were assessed visually between the categories complete break, CB, hinge break, HB, partial break, PB and no break, NB.

4.3.2 Tensile test

The tensile properties of the studied compounds were determined according to ISO 527-1 Plastics – Determination of tensile properties – Part 1: General principles. The standard specifies the general principles for the testing procedure, conditions and the test specimens. [101]

The tensile specimens were die cut from the produced 4 mm thick sheets by using a specific die for dumbbell shaped 1A test specimen according to ISO 527-2. Prior to testing the specimens were conditioned for at least 16 hours in the standard atmosphere and the tests were conducted in the same atmospheric conditions.

The tensile tests were conducted by using Zwick/Roell universal testing machine. At least 5 specimens were tested for each sample and the results are presented as the average of these 5 results. The test speed was 1 mm/min until the tensile modulus, that is, until the elongation of 0.25 % and after that the speed was 50 mm/min. The properties studied in the tensile test were tensile modulus (E_t), tensile stress (σ_M), stress at yield

(σ_Y), elongation at yield (ε_Y), stress at break (σ_B), elongation at break (ε_B), and nominal elongation at break (ε_{tB}).

4.3.3 Microscopy

The morphology of the studied compounds was analysed by optical microscopy and electron microscopy. The optical microscopy analysis was performed on the films produced from the selected compounds using the optical microscope Reichert –Jung Polyvar-Met. The analysed samples were prepared by cutting thin slices if the films perpendicular to the machine direction of the film. The film surface was characterized by using Nikon SMZ1500 optical microscope.

The morphology of the produced films was examined also by using field emission FEI Quanta 200 FEG scanning electron microscope operating at 7.5 kV. Prior to analysis the films were cryo-fractured under liquid nitrogen and the fracture surfaces were coated thinly with a gold/palladium alloy.

4.3.4 Melt flow rate

The Melt flow rate of the compounds was studied according to the standard SFS-EN ISO 1133-1 Plastics – Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics – Part 1: Standard method. The standard specifies the methods for determination of the melt mass flow rate (MFR) of thermoplastic materials under specific conditions of temperature and load. [102]

The measurements were conducted under 2.16 kg weight at the temperature of 230 °C. The melt flow rates of the compounds were analysed by measuring the weight of the extrudate coming through the die within 1.0 minute, taking an average on 3 measurements and multiplying the value by 10 to get the final value for the melt flow in 10 minutes.

4.3.5 Differential scanning calorimetry

The thermal properties of the compounds were studied by differential scanning calorimetry, DSC, according to the standard SFS-EN ISO 11357 Plastics. Differential scanning calorimetry (DSC). The standard specifies the methods for the thermal analysis of the polymers and polymer blends and it can be used for the observations of different physical transitions, such as glass transition, melting and crystallization, and the heat capacity. [103]

Prior to the DSC analysis the studied samples were homogenized by using the MFR device. The Mettler-Toledo Differential scanning calorimeter was used in the analysis of the thermal properties in nitrogen atmosphere with 50.0 ml/min flux and the device was calibrated against certified indium reference The samples were scanned at heating rate of 10.0 °C/min and heated from 30 to 225 °C and held at this temperature for 5.0 minutes to erase the thermal history during processing. The samples were then cooled at the rate of 10.0 °C/min until 30 °C and again after holding at this temperature for 5.0 minutes the samples were heated again until 225 °C following the same heating rate as on the first scan. The heat flow during the scans was recorded and the data was analysed by using STAR^e SW 8.10 thermal analysis software.

5. RESULTS AND DISCUSSION

The most important results obtained in the experimental part are presented in this chapter. The results are divided in following sections: visual observations, mechanical properties, morphology of the compounds and melt flow and thermal properties.

5.1 Visual observations

The pelletized compounds and neat polymers are presented in Figure 5.1. It can be seen already from the pellets how the colours of the compounds differ. The neat polymers PE, PA-L and PA-M and the matrix compounds PE-A and PE-B have a white, "natural" colour and the blends with the matrix compounds and the neat polyamides are slightly yellowish. The blends with recycled material have darker, brown colour.

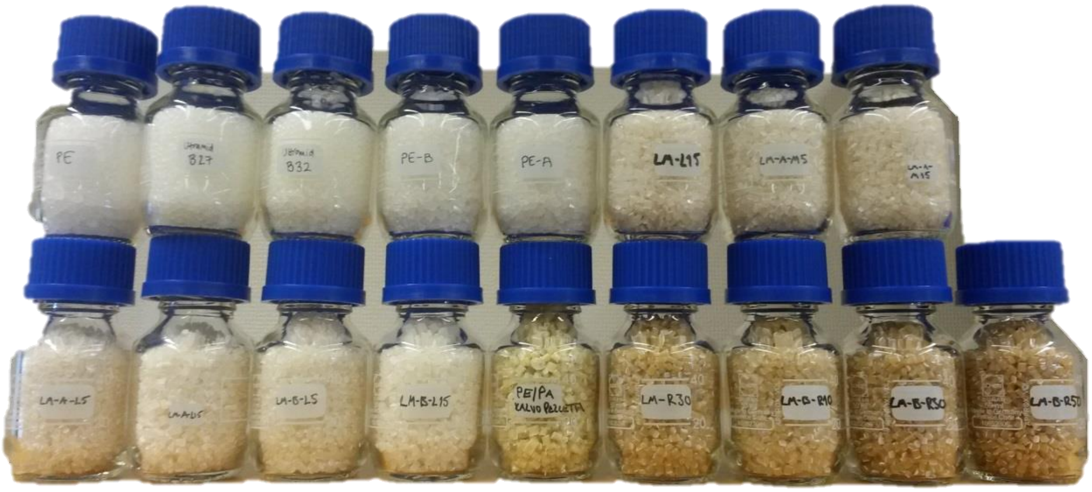


Figure 5.1 Pelletized compounds. Top row from left: PE, PA-L, PA-M, PE-B, PE-A, PE-L15, PE-A-M5 and PE-A-M15. Bottom row: PE-A-L5, PE-A-L15, PE-B-L5, PE-B-L15, R100, PE-R30, PE-B-R10, PE-B-R30 and PE-B-R50

After the pellets were compressed into sheets the evaluation of the colour was easier as the studied surface was larger. The same differences were observed as with the pellets, but in addition to the colour, the homogeneity of the colour was also possible to evaluate visually. The compressed sheets are presented in Figure 5.2.

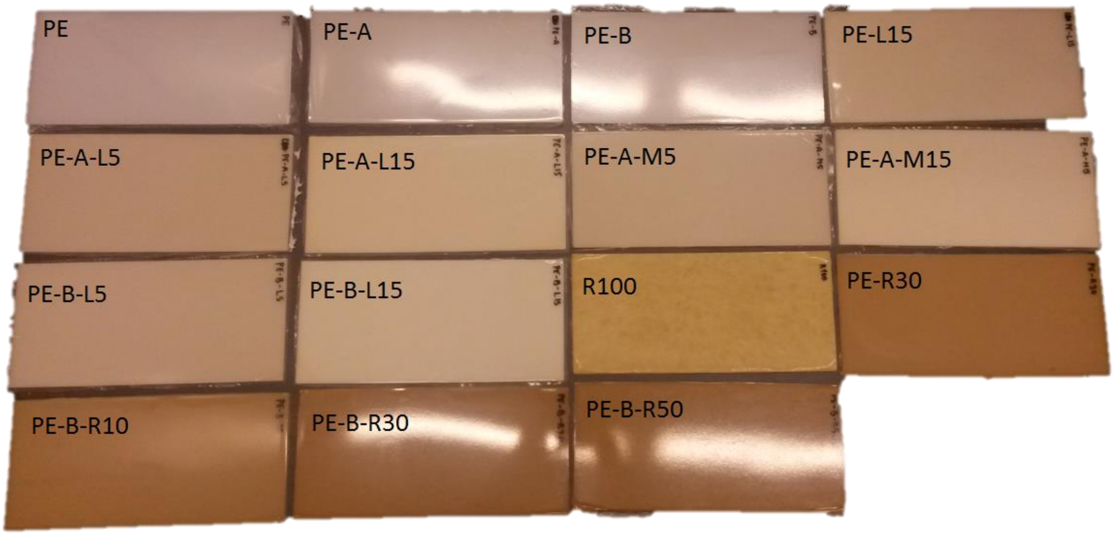


Figure 5.2 Compounds pressed into 16x35 cm sheets.

The colour difference between the compounds is amplified when compressed into sheets. The difference between the natural colour of the PE and matrix compounds and the yellowish colour of the virgin matrix/PA blends is obvious. It can also be seen in Figure 5.2 how the compatibilized compounds containing 15 wt.% of PA have a slightly lighter colour than the compounds containing only 5 wt.% of PA. The R100 blend consisting only of the recycled film material has a strong yellow colour with darker brown patches. The blends with the PE-B matrix and the recycled blend have the darker colour the larger the recycled content is.

The colouring of the compounds containing matrix compounds and neat PA is probably due to some type of material degradation and oxidation in the blend during compounding. The stronger the colouring of the compounds containing recycled material could be due to the degradation and oxidation of the unknown additives or tie-layers in the recycled blends, as the colour darkens by the increase of the content of the recycled blend.

The same type of uneven colouring as observed in the R100 recycled blend was observed the uncompatibilized blend on PE and 15 wt.% of low viscosity PA, but the colour differences in the blend were lighter. This uneven colour is an indication of heterogeneous blend morphology and lack of adhesion between the phases.

5.2 Mechanical properties

Mechanical properties of the compounds were characterized by Charpy impact test and tensile test. The results of these characterisations are presented and evaluated in following sub-sections.

5.2.1 Impact properties

The Charpy impact strength of the compounds was studied on notched specimens at room temperature and the results are presented in Table 5.1. The table gives the average of at least 10 parallel measurements and the observed break types. Most of the break types observed were partial breaks, PB, but also some hinge breaks, HB occurred. The sample preparation of the PA-L and PA-M turned out to be too complex task with the equipment available and therefore the impact strength for polyamide given in the table is obtained in the Ultramid B27 data sheet, that is, the PA-L, for conditioned and notched specimen.

Table 5.1 Charpy impact properties of the compounds

Material	Charpy Impact strength [kJ/m2]	Break type
PE	61	PB
PA	60*	
PE-A	65,8	PB
PE-B	62,4	PB
PE-A-L5	64,1	PB
PE-A-L15	40,6	PB
PE-A-M5	60	PB
PE-A-M15	31,3	PB
PE-B-L5	65,8	PB
PE-B-L15	66	PB
PE-L15	11,4	HB
R100	13,9	7 HB/ 3PB
PE-R30	52,2	PB
PE-B-R10	62	PB
PE-B-R30	52,1	PB
PE-B-R50	19,6	4 HB/ 6PB

*= value obtained in the Ultramid B27 data sheet

The impact strength of the neat PE and PA-L were really close to each other, 61 and 60 kJ/m^2, respectfully. The addition of CP in the PE matrix increased the impact strength, however, PE-A containing only 5 wt.% of CP resulted in impact strength higher than PE-B with 10 wt.% of CP in it. In general, the compatibilization of the compounds with virgin polymers enhanced the impact properties when compared to the uncompatibilized compounds. Figure 5.3 shows the comparison between the matrices containing different amount of CP as a function of low-viscosity PA content. Also the curve for the recycled blend comprising of PE-B and varying amount of recycled blend is presented in the graph. The data points of 0 % of PA represent the matrix compounds, that is, PE, PE-A and PE-B.

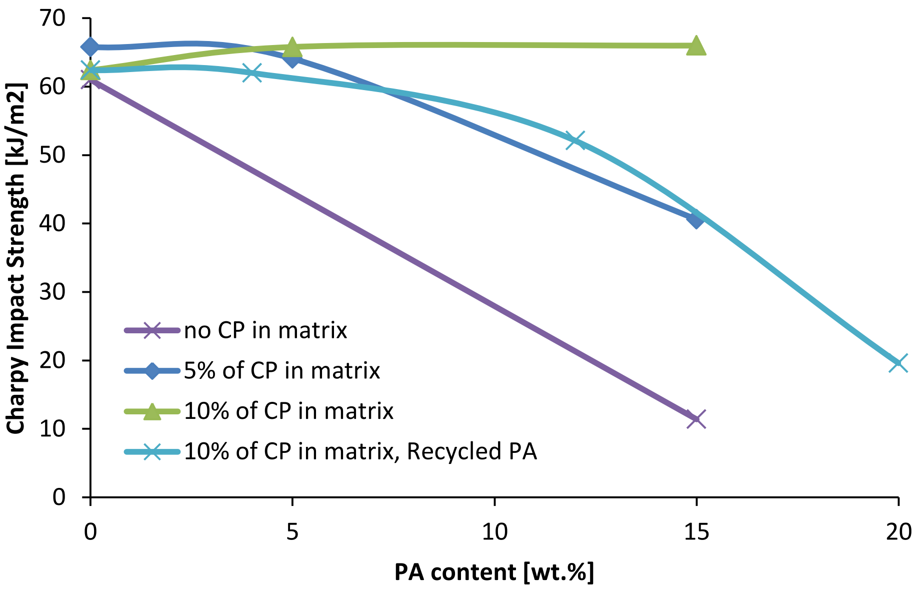


Figure 5.3 Charpy Impact Strength as a function of PA content

It can be seen in the Figure 5.3 that the uncompatibilized blend had a rapid decrease from 60 to 11.4 kJ/m^2 in the impact strength as the content of PA in the compound increased to 15 wt.%. This is most presumably due to the weak adhesion between the PE and PA phases and due to the inhomogeneous morphology of the compound. The compounds with PE-A matrix experienced also a loss in the impact strength with increased PA content: At PA content of 5 wt.% the strength had decreased only slightly, presumably due to the high CP/PA ratio in the blend an thus due to the successful compatibilization resulting from it. At 15 wt.% of PA the CP/PA ratio is only 1/3 of the PE-A-L5 and the impact strength has decreased almost 40% from that of neat PE-A matrix compound. With the PE-B matrix compounds the added PA in the blend seemed to increase the impact strength. Both blends, with 5 and 15 wt.% of PA had the impact strength of approximately 66 kJ/m^2 which is about 6% higher than that of the neat PE-B matrix. The studies of Burgstaller et al. [9] support these observations of rapidly decreasing impact strength of uncompatibilized PE/PA blend with increasing PA content (up to 20 wt.% of PA) and the slowly increasing or decreasing impact strength of the compatibilized blends, depending on the compatibilization method. However, the neat PA used in their studies exhibited significantly higher impact strength than that of PE they used, and even in the case with increasing impact strength with increasing PA content the measured values were merely following a linear increase towards the values of neat PA and no values over this imaginary line is observed. This is interesting because in the compounds studied in this thesis the impact strength of the some of the produced compounds is higher than those of any the blend components.

When the compounds with 15% of PA are compared, already 5% of CP in the matrix gives an increase of approximately 250% in the Charpy impact strength and 10 % of CP in the matrix increases the impact strength from the non-compatibilized blend almost

480%. The reason for this is in the toughening effect of the small dispersed PA droplets, and with finer structure and increased adhesion between the phases as the impact resistance is higher than for the less compatibilized blends with larger dispersed particles and possibly smaller adhesion between the phases to prevent the crack propagation.

It can be also argued if the compression moulding method of the test specimens with the compression temperature 10 °C lower than the actual melting temperature of PA has some effect on the impact properties. As some parts of the PA phase are not molten during the compression moulding this could have an effect on the flow properties of the blends as it takes the form of the mould and thus on the morphology. It is also possible that if the morphology formed during compounding was not stable the subsequent heating would stabilize the structures and for example some coalescence of the PA droplets could occur. This effect, however, is present in all samples as the compression process was the same for all the compounds.

The compounds with the PE-B matrix and the recycled material as the minor phase showed a decrease in the impact strength with the increased content of the recycled material, and thus also by the increasing PA content. A comparison between all the blends containing recycled material is presented in Figure 5.4. In general the dominating effect of the matrix material is well seen as by the increasing content of the recycled material the impact strength decreases. The compound with the least recycled content (and least PA) is PE-B-R10 and it has the highest observed impact strength of the recycled compounds, that is, 62 kJ/m^2. This is about the same than that of the matrix compound PE-B, which indicates that small amounts of the recycled material in the matrix do not affect the impact properties. 30 wt.% of the recycled material in the compound resulted in approximately 15 % lower impact strength than the neat PE. Despite the prominent difference in the PA content the recycled blend R100 with about 40 wt.% of PA in it results in impact strength of 13.9 kJ/m^2 which is still over 20 % higher than the impact strength of the uncompatibilized PE-L15. Also the PE-B-R50 with PA content of approximately 20 wt. % has almost double the impact strength than that of PE-L15.

The compatibilization of the recycled blend showed little effect as the compatibilized and uncompatibilized blends with 30 wt.% of the recycled blend had the same impact strength with each other. The impact strength of the compounds was about 14 % smaller than with virgin PE. The lack of difference between the compatibilized and uncompatibilized blends could be due to the adhesive materials already present in the recycled film material which could possibly also act as some sort of compatibilizing agents in the blend and thus no extra CP would be needed to stabilize the morphology.

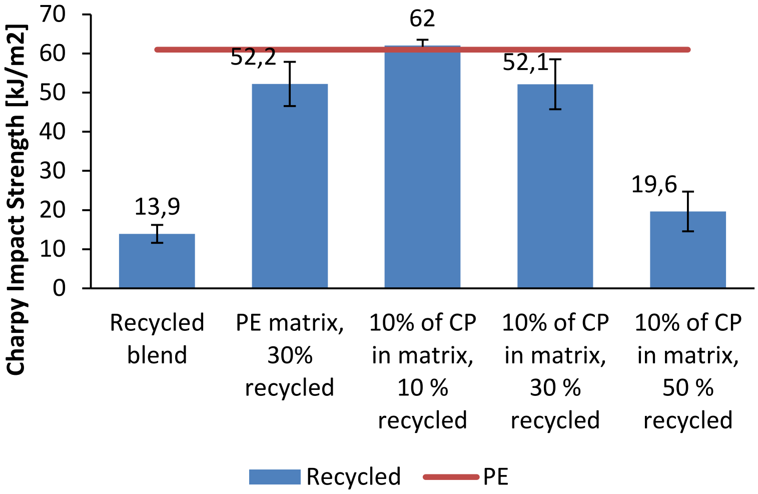


Figure 5.4 Charpy impact strength of blends containing recycled material

When the impact strength of the studied compounds is presented as a function of the CP/PA ratio, a different type of comparison between the virgin and recycled materials can be done. As presented in Figure 5.5 the trends of the data points of both virgin low viscosity PA and recycled PA from the recycled film material are approximately the same, the virgin PA only gives slightly higher values especially at low CP/PA values. For example at CP/PA ratio a bit over 0.5, that is twice as much PA than CP in the compound, containing recycled PA gives only 52.1 kJ/m^2 impact strength whereas compound with PA-L results in 66 kJ/m^2. The higher the CP/PA ratio is the closer the impact strength values are the values of PE. This was expected because with high CP/PA ratio there is significantly more CP than PA and therefore there is also significantly more PE in the compound as the CP is part of the matrix compound. This analysis, however, does not take into account the possible additional adhesives in the recycled blend which would increase the CP/PA ratios for the recycled blend. It can, however, be said that within the measurement inaccuracies trend is similar for both cases.

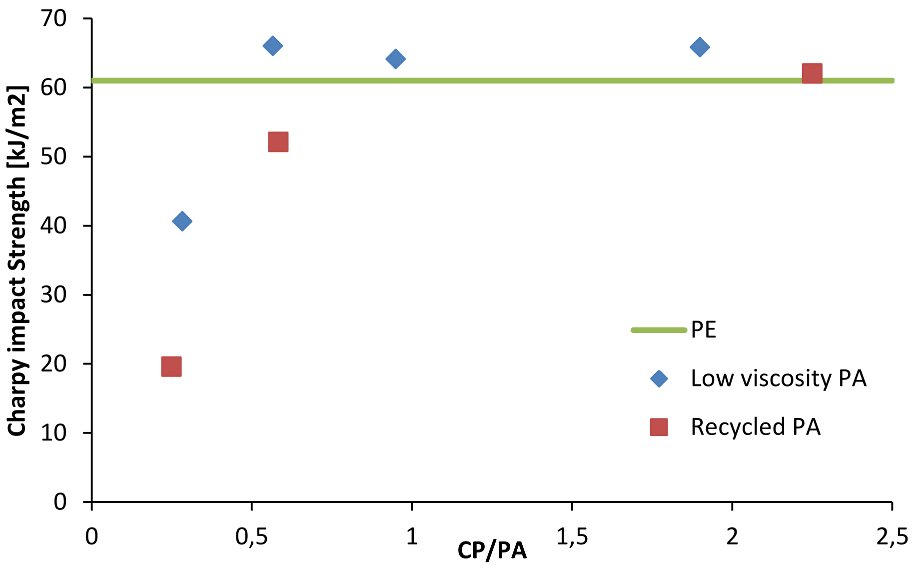


Figure 5.5 Charpy impact strength of the compounds as a function of the weight ratio of compatibilizer precursor to polyamide

The effect of the viscosity of polyamide is presented in Figure 5.6. The compounds of PE-A with 5% of CP and two different polyamides with different melt viscosities, PA-L with low melt viscosity and PA-M with medium viscosity were studied. The compounds with PA-L showed smaller decrease in the impact strength with increased PA content than the compounds with the medium viscosity PA-M.

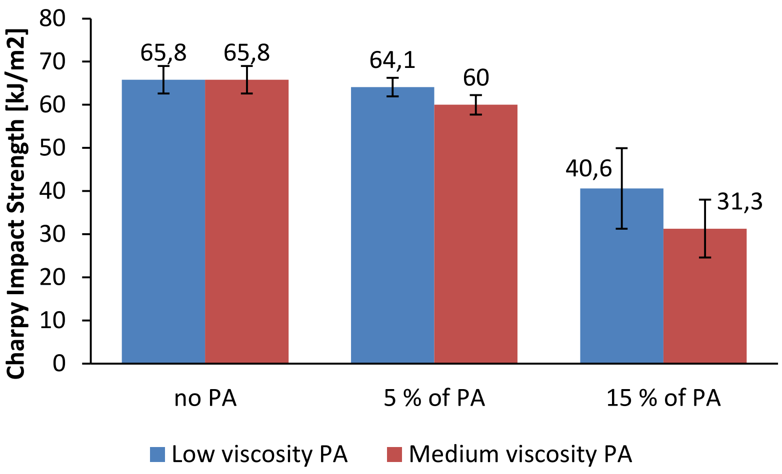


Figure 5.6 Charpy impact strength of the compounds containing 5 wt.% of CP and low viscosity PA or medium viscosity PA

With mainly linear PA6 the lower viscosity is usually related to smaller molecule weight. This means that with the same weight of low and medium viscosity polyamides the lower viscosity PA has shorter chains and thus higher concentration of the $-NH_2$ amine end groups. These groups can therefore potentially form more bonds with the anhydride moieties in the CP and thereby form the compatibilizing graft copolymers.

And hence, the better impact properties of the compounds with lower viscosity PA could be explained.

Altogether, the virgin polymers PE and PA-L exhibited rather similar impact strength. The addition of PA to uncompatibilized PE matrix decreased the impact properties drastically. The compatibilization of the blends decreased the loss if impact strength by increasing PA content for the compounds with only 5 wt.% of CP in the matrix and for the compounds with the recycled material as the minor phase. The virgin compounds with PE-B showed higher impact strength than those of neat PE or PA which owes presumably to the high interactions between the phases due to the formation of compatibilizer at the phase interface and the reinforcing effect of the small PA droplets in the PE matrix. The blends with recycled material did not show any effect with the addition of CP in the compound. The most significant factor for the impact properties seemed to be the CP/PA ratio which followed the same trend, no matter if the PA in the blend was virgin or recycled.

5.2.2 Tensile properties

The tensile properties of the prepared compounds were studied according to the procedure described earlier. The obtained effects of the blend composition on the tensile modulus (E_t), ultimate tensile strength, that is, the maximum stress (σ_M), nominal strain at break (ε_{tB}), stress at yield (σ_Y), elongation at yield (ε_Y), stress at break (σ_B), and strain at break (ε_B) are presented in Table 5.2. The results show that the increasing PA content stiffens the material as tensile modulus and stress at yield increase by increasing PA content. At the same time the tensile strength and the strains at yield and break decrease.

Different types of behaviour under tension were obtained in the tensile tests and some examples of the typical stress – strain curves obtained are presented in Figure 5.7. The scale of the different tensile behaviours was broad ranging from rigid recycled R100 blend breaking just after yielding to compound PE-A-M15 with the max stress achieved at yield and further on to the highly stretchy behaviour of PE and the matrix materials PE-A and PE-B which did not break even at the strain of 800 % but slipped away from the clamps of the testing machine as the tensile specimens thinned duo to the excess strain.

Table 5.2 Tensile properties of the compounds

Material	Tensile Modulus [MPa]	Tensile strength [MPa]	Nominal Strain at break [%]	Stress at Yield [MPa]	Strain at Yield [%]	Stress at Break [MPa]	Strain at Break [%]
PE	342	24,5	800	11,3	14	24,5	800
PA	1000*		50*	45*	20*		
PE-A	350	23,8	790	11,4	14	23,8	800
PE-B	357	24,2	820	11,5	14	24,2	830
PE-A-L5	428	20,1	590	12,2	11	20,1	590
PE-A-L15	504	15.3	410	13,26	10,6	15,26	412
PE-A-M5	415	22,2	700	12,1	11	22,2	710
PE-A-M15	513	13,3	270	13,3	10	11,9	270
PE-B-L5	410	21,9	690	12,1	11	21,9	700
PE-B-L15	488	17	420	13,3	10	17	430
PE-L15	524	13,2	8,9	13,2	6,9	12,9	10
R100	436	11,7	19	11,7	20,4	11,7	23
PE-R30	424	15,5	440	12,3	13	15,5	450
PE-B-R10	372	23,2	760	11,6	13	23,2	760
PE-B-R30	410	15,6	450	12,1	14	15,6	450
PE-B-R50	450	12,9	71	12,9	15,1	11,7	76

*= value obtained in the Ultramid B27 data sheet

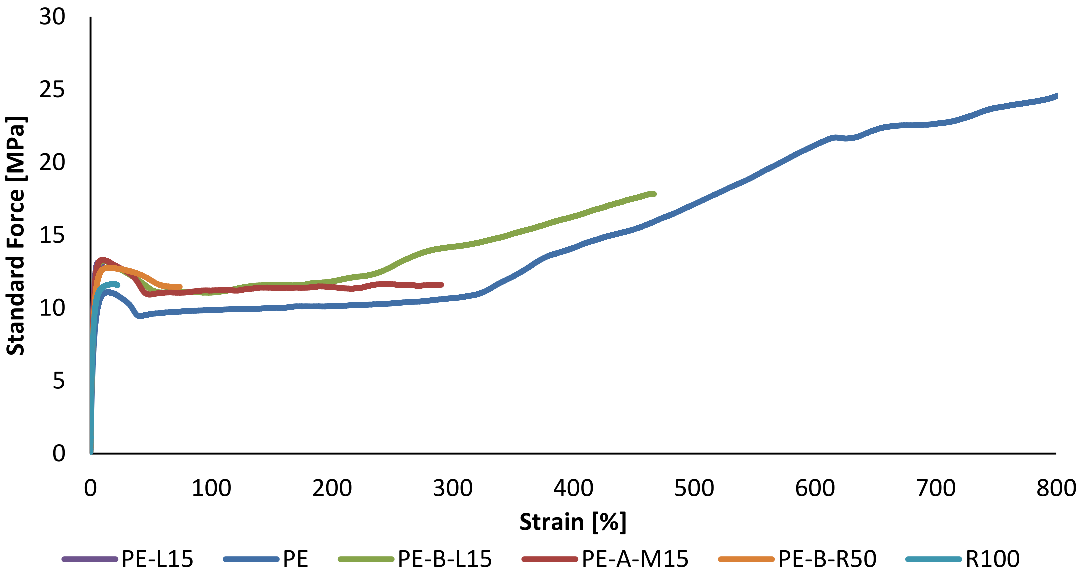


Figure 5.7 Typical stress - strain curves for tensile tests

Figure 5.8 presents the tensile modulus as a function of the content of PA-L or the recycled PA. All matrices exhibited E_t around 350 MPa. The increase of the tensile modulus as a function of PA content was rather linear, and no significant differences between the different matrices were observed. When the observed E_t values are compared to the neat PE the addition of 15 % of PA increased the tensile modulus with 43 % with 10 % of CP in the matrix, 47 % with 5 % of CP in the matrix and up to 53 % without any CP. This means that the uncompatibilized blend is slightly more rigid and the addition of CP increases the elasticity of the compound by decreasing the tensile modulus. The results of increasing tensile modulus by increasing PA content in compatibilized and uncompatibilized blends are supported by the reported results of Burgstaller et al. [9]. Their findings, however, showed that the blends compatibilized with PE-g-MA compatibilizer precursor followed the same trend as the uncompatibilized blend, which is not totally in alignment with the results in this thesis, even though, the observed difference was rather small. Filippi et al. [11], on the other hand, have reported on the same type of decrease in the tensile modulus when the PE/PA ratio is kept constant and the only the content of CP is increased.

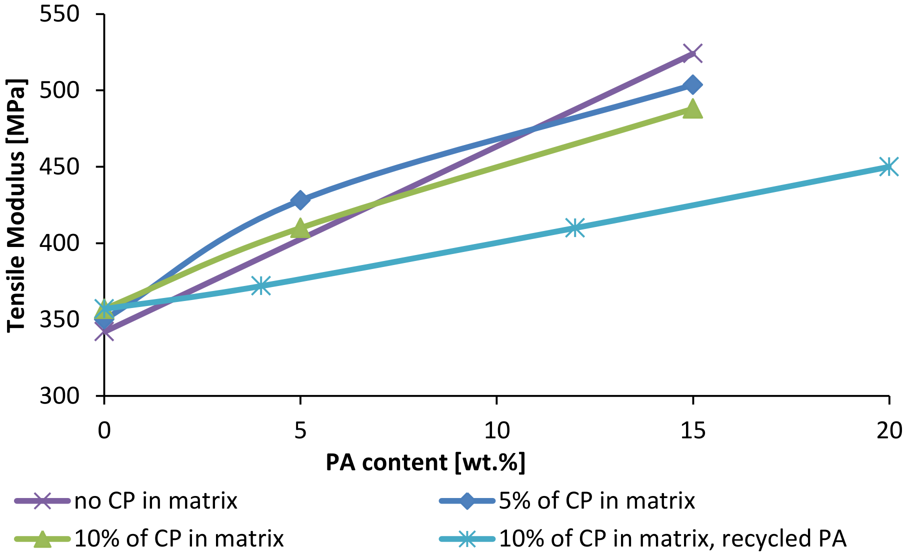


Figure 5.8 Tensile Modulus as a function of PA content

The compounds containing recycled material did not show the same amount of increase in the tensile modulus as the blends with virgin material, as shown in Figure 5.8. The interpolated value for the PA content of 15 wt.% is approximately 430 MPa which corresponds to only 26 % increase to the virgin PE and is about half of the increase obtained in the uncompatibilized compound with equivalent amount of PA. Even the compound containing 20 % of recycled PA, E_t=450 MPa, does not reach the tensile modulus values of the compounds with virgin materials at PA content of 15 wt.% of PA. This is probably due to the LDPE and LLDPE in recycled blend which normally exhibit lower E_t and therefore have their own contribution to the properties of the blend.

The stress at yield and strain at yield of all the compounds with virgin materials follow the same trends, as shown in Figure 5.9 and Figure 5.10. The stress at yield increases fairly linearly as a function of PA content from about 11.5 MPa with the pure matrix materials until 13.3 MPa with 15 wt.% of PA. The compatibilization of the virgin blends shows no effect on σ_y. The strain at yield of the uncompatibilized blend decreases by 50 % with the addition of 15 wt.% of PA. The addition of CP stabilizes the structure slightly and the decrease is only about 30 %. However, it has to be remembered that the elongation at yield is measured in percentage and as the measured elongations are small, already a difference of 1 or 2 percentage points makes a significant difference.

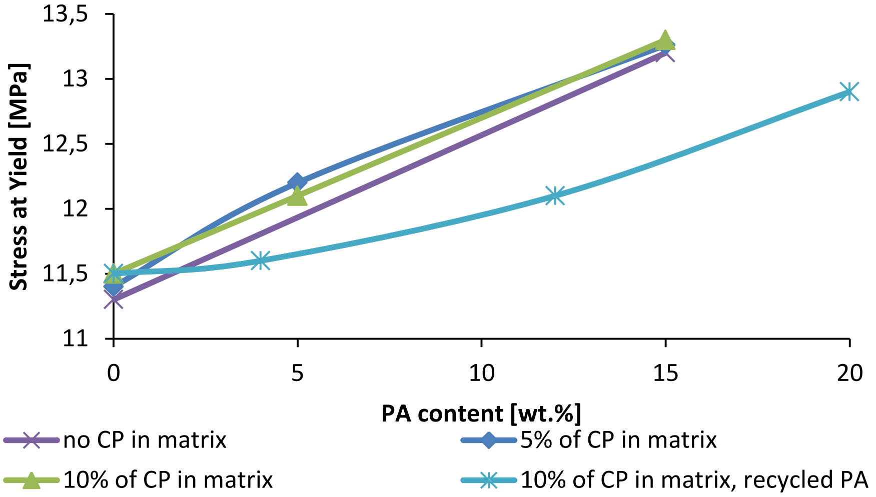


Figure 5.9 Stress at yield as a function of PA content

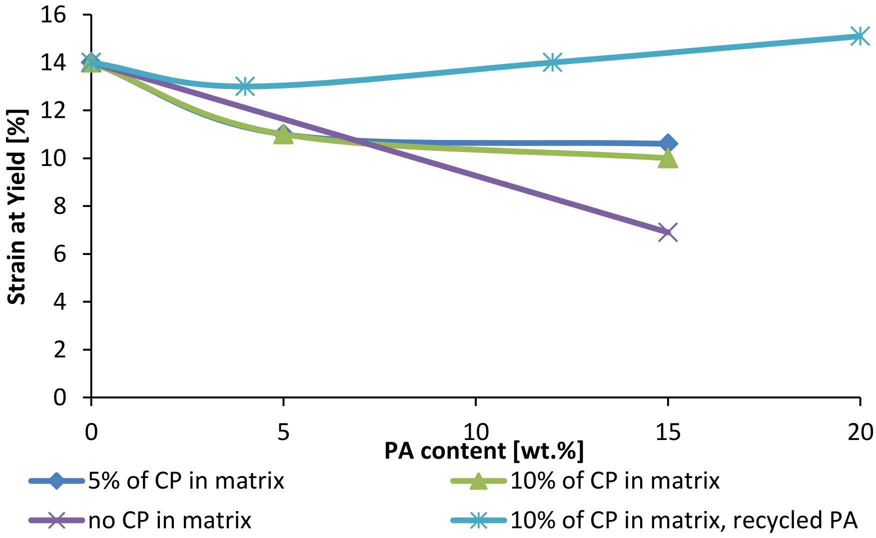


Figure 5.10 Strain at yield as a function of PA content

The compounds with recycled material differ by the stress at yield and strain at yield behaviour from the blends with virgin materials. The stress at yield increased by the increase of the PA content more moderately and for example the same stress at yield values achieved with the addition of only 5 % of virgin PA are reached with recycled material with approximately 12 wt.% content of PA. With the 50/50 blend of PE-B and recycled material the PA content is about 20 wt.% and the strain at yield is 15 %, which is even higher than those of matrix materials. The differences between the virgin and recycled compounds are again probably due to the other polymers in the recycled blend which affect the blend behaviour more than for example compatibilization. Araújo et al. [4] named the stress at yield as a limiting property and therefore proportional to the degree of adhesion in the blend interface. In their studies they observed increased yield stress with the use of CP, which is opposite to the observations in this thesis. The results observed in this thesis follow more the behaviour of uncompatibilized blend observed in the studies on Araújo et al. Based on their conclusions this indicates a lack of adhesion between the phases as the compatibilizer has not localized on the interfaces. The recycled blends, on the other hand show increased yield stress, which support the findings of Araújo et al.

The strain at break and the ultimate tensile strength of the studied compounds decreased both by the increased polyamide content as shown in Figure 5.11 and Figure 5.12. The decreasing rate of the compatibilized blends and the blends with recycled material were approximately the same, whereas the uncompatibilized blend showed prominently faster decreasing rate as the addition of 15% of PA resulted in 10 % strain at break. The compatibilization of the blends increased the maximum strain of the 85/15 PE/PA blend from 10 to over 400 %. Filippi et al. [11] demonstrated the similar type of significant increase in elongation with the addition of CP when 75/25 LDPE/PA6 blend was studied. The compatibilization of the blends was suggested to enhance the interfacial adhesion in the compatibilized samples and, thus, increase the observed strains.

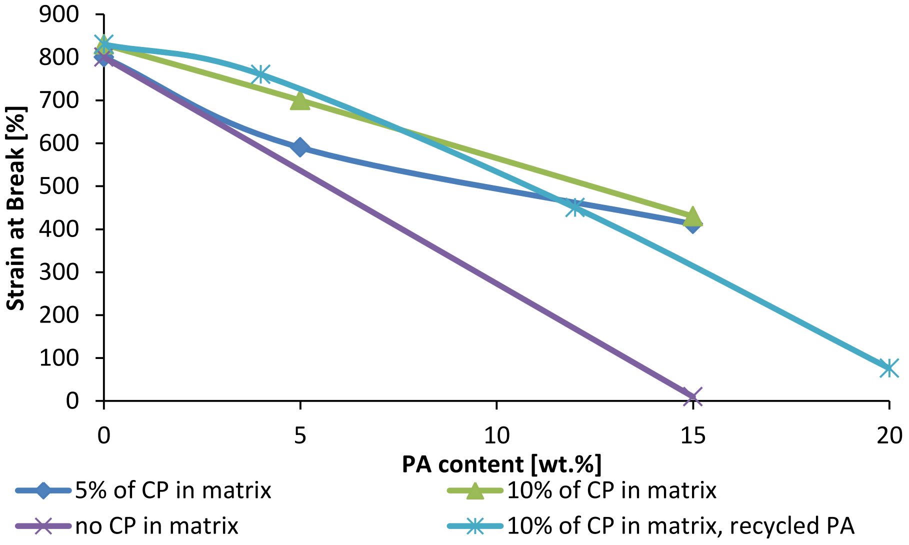


Figure 5.11 Strain at break as a function of PA content

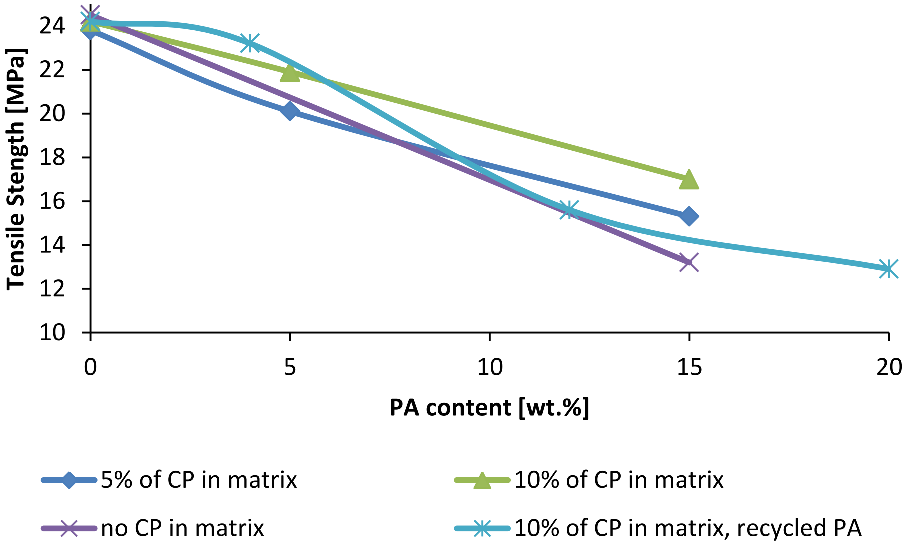


Figure 5.12 Ultimate tensile strength as a function of PA content

The tensile strength of the studied compounds also seemed to increase when CP was added in the blend. The 30 % increase in tensile strength with the addition of 10 wt.% of CP in in the matrix of a 85/15 PE/PA blend is rather large when compared to those minor changes reported by Filippi et al. [11] and Burgstaller et al. [9]. They reported of both increase and decrease in σ_M depending on the compatibilizer used in the system, but the differences were only some percentages. However, the amount of CPs used in studies of Filippi et al. was smaller than that of used in this thesis, which should explain the minimal differences in studies of Filippi et al. In studies of Kelar and Jurkowski [18] the increasing PA content of a compatibilized blend was reported to increase the tensile strength which does not support the findings in this work. A decrease in the tensile strength was reported to occur only on the compatibilized compound extruded with a shaping head and without any further mixing, which was taken as an indication of unformed compatibilizers.

The comparison between the different compounds containing recycled material is presented in Figure 5.13a-e. The red line in the figures represents the corresponding value for the virgin PE. Figure 5.13a shows the tensile modulus of all compounds containing recycled material. As already noted, the change in the modulus is rather linear with increasing content of the recycled material. Even though the PA content of R100 is higher than that of the PE-B-R50 the latter has the higher tensile modulus from these two samples. In general, the tensile properties of PE-B-R50 are rather similar to R100, only the stress at yield was approximately 10 % higher and the strain at yield about 25 % smaller than those of R100.

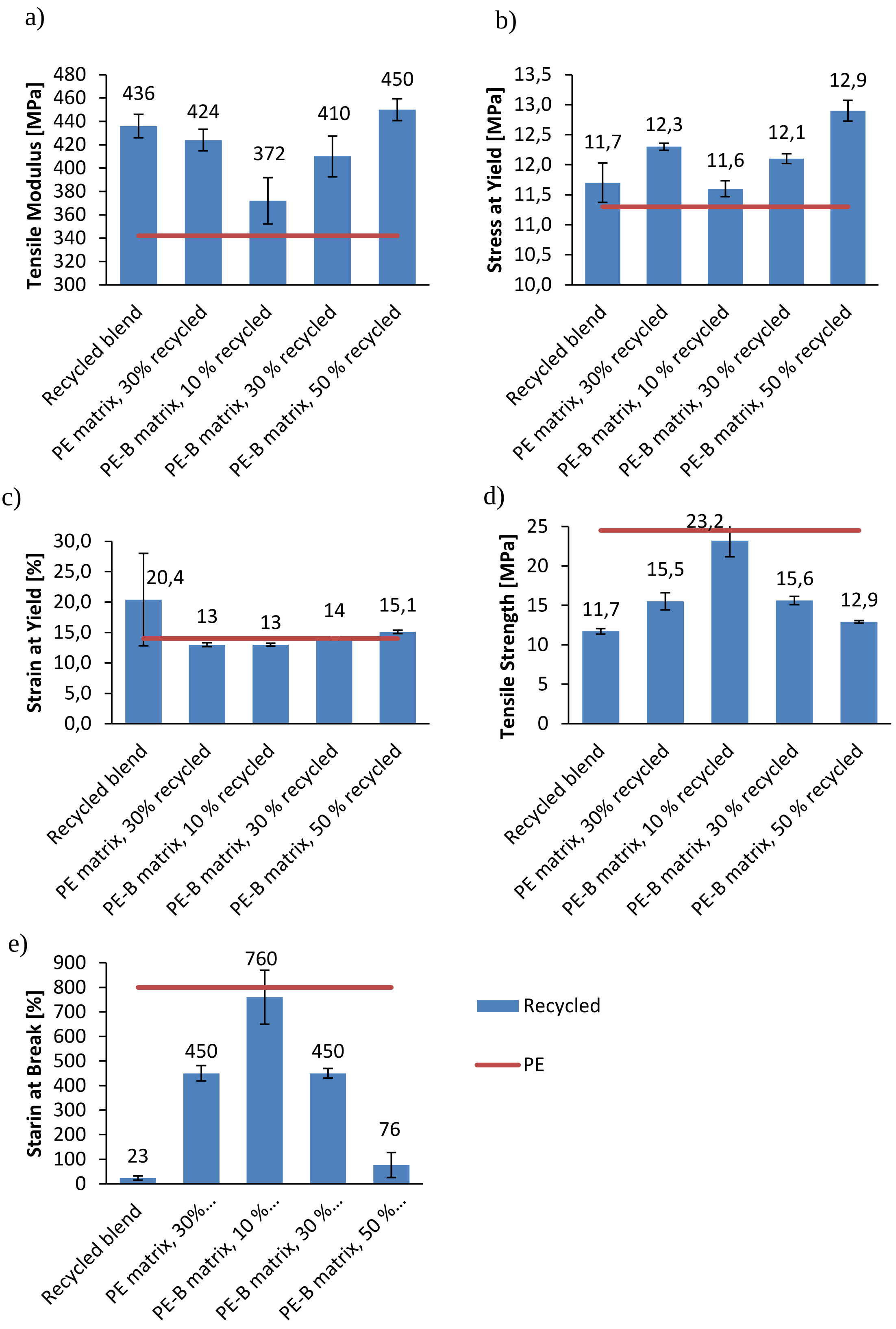


Figure 5.13 Tensile properties of the blends with recycled material (a) Tensile Modulus, (b) Stress at Yield, (c) Strain at Yield, (d) Tensile Strength and, (e) Strain at Break

The most significant observation in the results presented in Figure 5.13 was again the lack of difference between the tensile properties of the compatibilized and uncompatibilized compounds containing 30 wt.% of recycled materials as for example the tensile modulus of the un-compatibilized blend was only about 3% higher than the corresponding value for compatibilized blend. Therefore, it can be said that the differences between the compatibilized and uncompatibilized 70/30 PE-B/Recycled material blends are negligible.

The tensile properties were also evaluated in the relation to the CP/PA ratio of the compounds. Figure 5.14 represents the tensile modulus (Figure 5.14a), ultimate tensile strength (Figure 5.14b), stress at yield (Figure 5.14c), strain at yield (Figure 5.14d) and strain at break (Figure 5.14e) as a function of the CP/PA ratio. The PA content was calculated for the compounds containing low viscosity PA and for the blends containing recycled material. As before, the PA content of the recycled material was assumed to be approximately 40 wt.% and, thus, for example the PA content of the PE-B-R30 blend was around 12 wt.%.

The graphs in Figure 5.14 show that the recycled and virgin PA follow about the same trends as the other in all but one tensile property, that is, the strain at yield, in which the blends containing recycled PA seem to yield at somewhat higher strains than the blends containing virgin PA-L. The tensile strength and strain at break seem to increase as the CP/PA ratio increases. In other words, the more there is CP in the blend and less there is PA the higher the strain at break or tensile strength are. The low CP/PA ratio results in small strains and lower tensile strength. However, usually the content of PE increases at the same time as the amount of CP and thereby the ratio of PE/PA might also affect the result. In tensile modulus, stress at yield and strain at yield the obtained values seem to be rather unaffected by the CP/PA ratio. However, at the CP/PA values under 1, that is, more PA than CP there is more deviation. At CP/PA values closer to 2 there is twice as much (when measured in weight) CP than PA which means with the amounts used in the studied blends that the overall content of the PA in these blends are relatively low and thereby the PE content is naturally high. Thus, it is expected that the properties are close to that of PE.

When the blends with PA-L and PA-M as a minor component in the compound were compared, no significant differences were obtained. The tensile properties of the compounds comprising of PE-A matrix material and 5 or 15 % of polyamide are presented in Appendix B. The only noticeable differences are in the maximum properties, that is, the ultimate tensile strength and strain at break. In these both the compounds with 5% of PA the medium viscosity PA yields in higher values than the low viscosity PA whereas with 15 % of PA the PA-L gives higher values than PA-M. However, the deviations of the results are in a range that could make these differences rather small if both in their upper and lower limits, respectively.

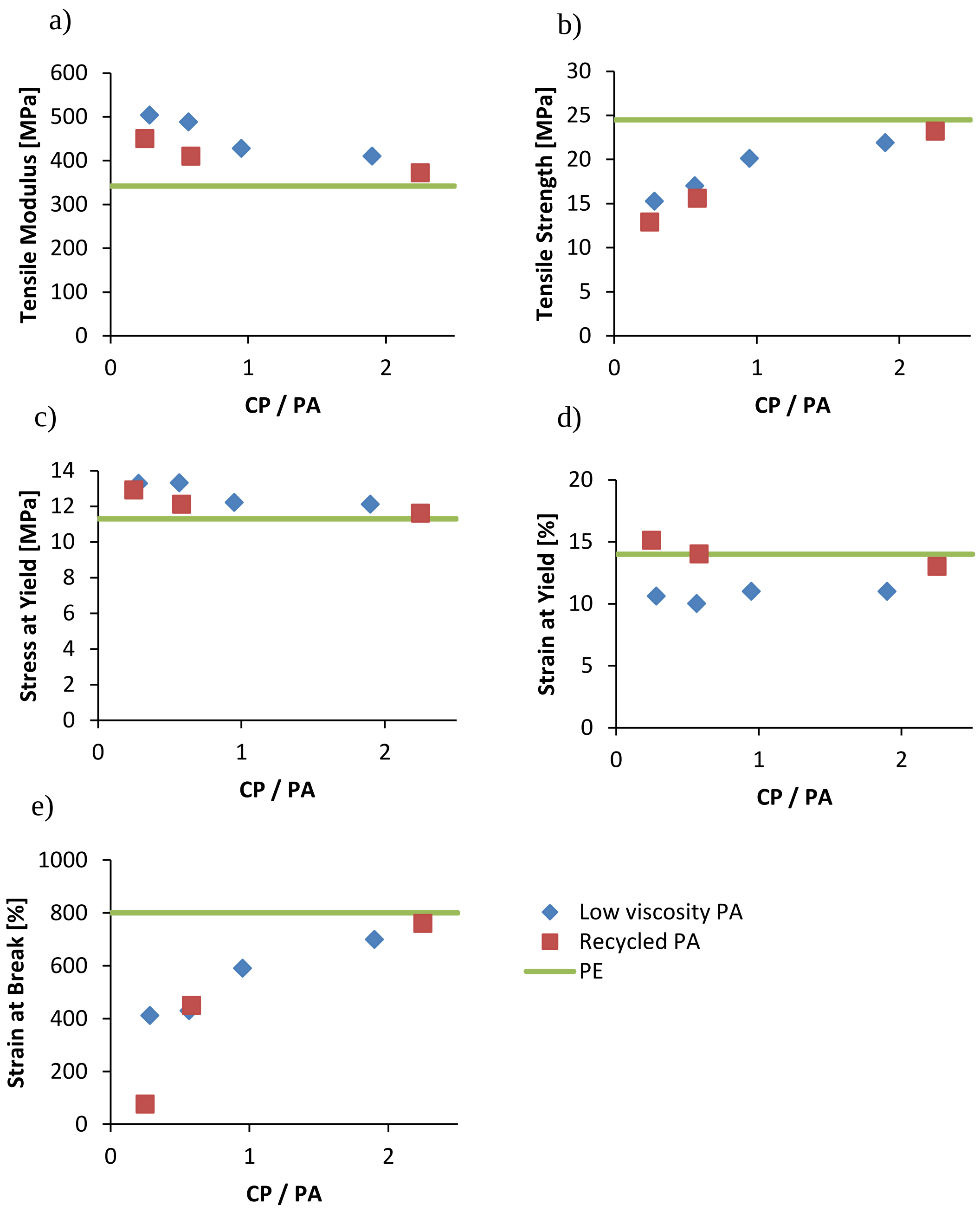


Figure 5.14 Tensile properties as a function of CP/PA ratio (a) Tensile Modulus, (b) Tensile Strength, (c) Stress at Yield, (d) Strain at yield and (e) Strain at Break

In general, the tensile properties show a strong dependence on the PA content and no matter if the blend is compatibilized or uncompatibilized. The increased mechanical properties by the addition of CP are an indication of a successful compatibilization of the virgin compounds. However, the content of CP did not show a big effect on the tensile properties as the compounds with PE-A and PE-B matrices resulted in rather identical results. The recycled materials did not show any significant differences between the compatibilized and uncompatibilized PE matrix.

5.3 Morphological analysis

The effect of the CP content on the blend morphology was evaluated from a selection of compounds converted into a form of film. The morphology of the selected compounds containing 15 wt.% of PA or 30 wt.% of the recycled material was analysed by using light microscopy and SEM analysis. In general, the all the studied compounds showed a morphology in which polyethylene was the continuous phase and polyamide phase was dispersed in droplets of varying size. Due to the cast film manufacturing process the droplets had a string-like shape oriented in machine direction. Some SEM images of the string-like PA droplets are presented in Appendix B. The orientation and shape of the PA droplets can also be seen Figure 5.15 presenting LM images of the film surface.

Figure 5.15 Light microscope images of the orientation and size variation of the PA droplets on the film surface with 112.5-fold magnification

Figure 5.16a-d presents the cross section images obtained by light microscopy, LM and Figure 5.17a-g presents SEM micrographs of the cryo-fractured fracture surfaces with 5000-fold magnification. Both sets of images clearly demonstrate the reduction in the size of the dispersed PA droplet in the matrix when CP is added in to the virgin compound, as expected. Figure 5.16a and Figure 5.17a of the binary, uncompatibilized PE-L15 blend show the large dimensions for dispersed PA droplets. With 5 wt.% of CP in the matrix the diameters of the PA droplets are smaller than when compared to the images of the uncompatibilized PE-L15, as seen in Figure 5.16b and Figure 5.17b. As the CP content increases more, the size reducing effect is even stronger, as shown in Figure 5.16c and in Figure 5.17d.

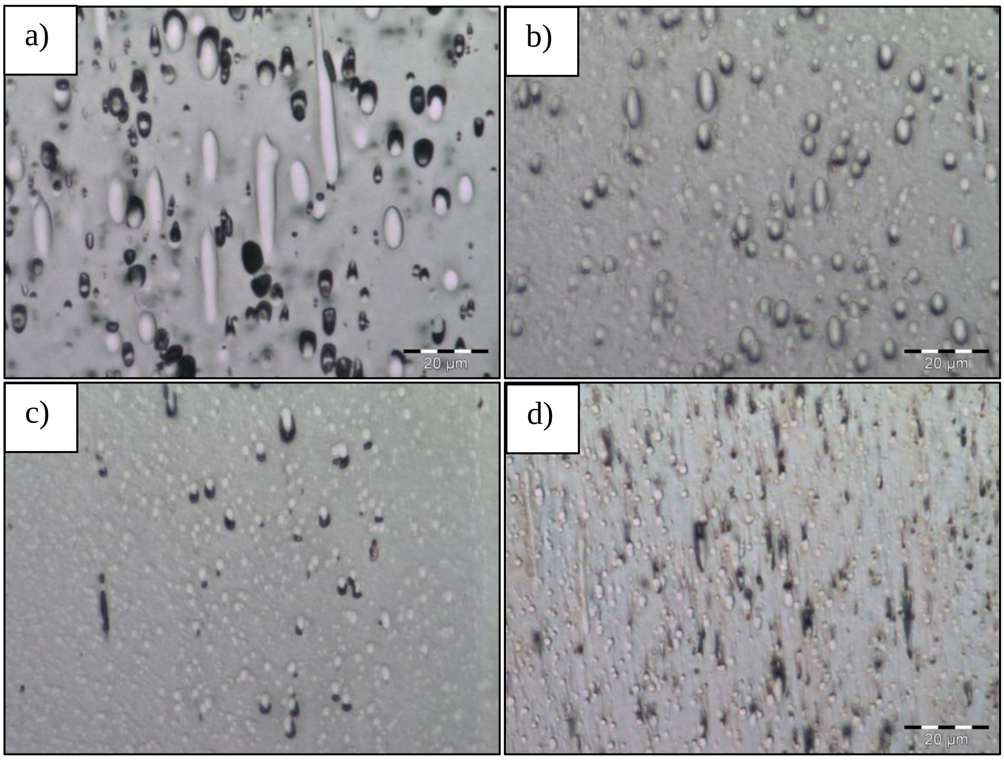


Figure 5.16 Light microscopy images of the film cross sections of (a) PE-L15, (b) PE-A-L15, (c) PE-B-L15 PE and (d) PE-B-R30

There are also some indications of weak adhesion between the phases. This is evident for example in the large black areas around the PA droplets in the LM images in Figure 5.16 representing air. However, the origin of the air in the LM images is not clear as it can be derived from the vaporized moisture in the PA phase or from the sample preparation during cutting. As no excess air was observed in the SEM micrographs between the matrix and dispersed phase, the sample cutting would perhaps be a more potential reason. Also the smooth surfaces of the PA droplets and the voids in the spots where the droplets have separated from the matrix, as seen in the SEM micrographs are indications of weak adhesion. The signs of weak adhesion seem to decrease as the CP content in the matrix increases. With 5 wt.% of CP in the matrix less air is observed in the cross sectional LM images than in the uncompatibilized blend, and fewer voids and partly pulled out droplets are present on the fracture surface of the SEM images. The Figure 5.17b of PE-A-L15 shows also the smooth surface of the exposed PA droplets. Despite the smaller droplet size the PE-B-L15 with 10 wt.% of CP in the matrix shows also some pulled out droplets and voids, as seen in Figure 5.16c and in Figure 5.17d.

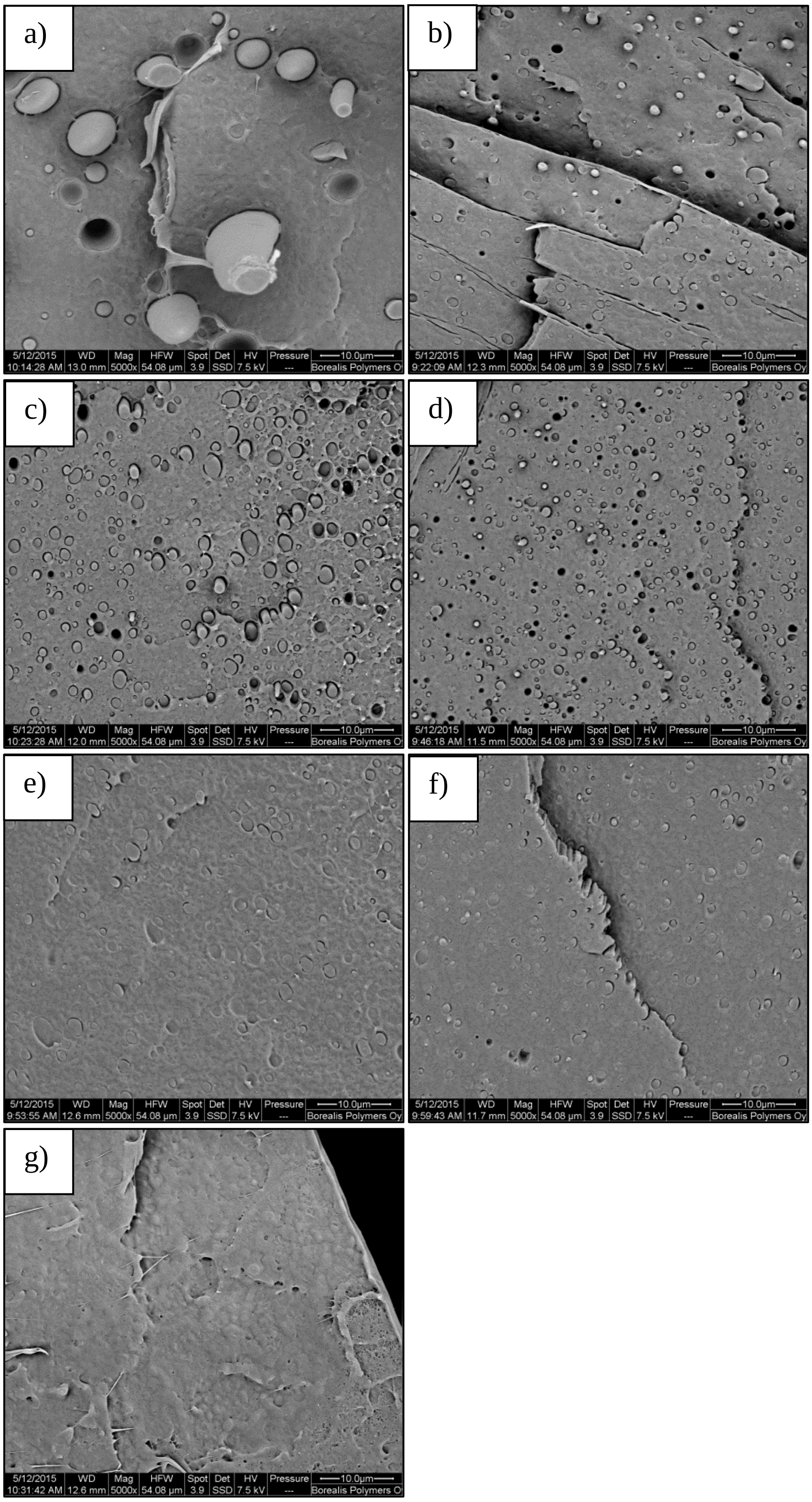


Figure 5.17 SEM micrographs of cryo-fractured fracture surfaces of (a) PE-L15, (b) PE-A-L15, (c) PE-A-M15, (d) PE-B-L15 PE, (e) PE-R30, (f) PE-B-R30 and (g) PE with 5000x magnification

As the mechanical characterisation already indicated, no evident difference between the uncompatibilized and compatibilized recycled blends was observed, as seen in Figure 5.17e and f. The dispersed droplet size corresponds approximately to that of in the compound PE-B-L15, which is demonstrated better in the LM images. The SEM micrographs, on the other hand, shows a smooth fracture surface with almost none voids or pulled out droplets, which indicates strong adhesion between the PA and the PE matrix. This is surprising, because the compound PE-R30 does not contain any added CP in the blend, and also because the addition of CP does not have any effect on the morphology. As already suggested in the context of mechanical tests the adhesive material in the recycled blend could have taken the role of a compatibilizer precursor and thus the added CP is excess. This would also explain the small particle size observed in both uncompatibilized and in compatibilized blends as the adhesive reduces the particle size and increases the interfacial adhesion.

Another reason for the fine morphology of the uncompatibilized recycled blend and for the lack of change as CP is added in the compound could also be in the degraded and oxidized blend components in the recycled material. The darker colour of the blends with recycled material was earlier suggested to occur due to the degradation and oxidation of some blend components originating from the additional processing steps of the recycled material. As Araújo et al. [4] demonstrated the polar groups of recycled PE formed in the oxidation can also form chemical bonds with PA and thus compatibilize the blends of PE and PA. If the amount of oxidised substances in the compound is high enough, no excess CP is needed to compatibilize the blend and thus this would explain why also the uncompatibilized blend exhibits a fine morphology and the same properties as the compatibilized compound.

In general the observed droplet size of the dispersed phase in uncompatibilized and compatibilized blends, is larger than that of reported by many papers concerning compatibilized blends of polyethylene and polyamide, for example by Filippi et al. [11] and Jiang et al. [16]. For example, in studies of Filippi et al. the observed average droplet diameter was in uncompatibilized 75/25 LDPE/PA6 blend 1.6 μm and already addition of 1 % of CP into the blend decreased the diameter to approximately 0.5 μm. Even though no quantitative analysis was not conducted on the droplet size in this theses, it can be said by visual observation that the observed droplets are larger that reported by Filippi et al. An explanation for this could be in insufficient mixing during compounding. This is supported by Kelar and Jurkowski who reported [18] of a larger droplet size and weaker adhesion between the phases in a compatibilized blend which was extruded with shaping head and without any further mixing and they suggested that the reason for this would have been the unformed PE-g-PA compatibilizer. However, as a reactive twin screw with specialized mixing modules was used when compounding, a sufficient dispersion and distribution should have been achieved also in this study. It is also possible that the conversion in to films affected the unstable morphology and the smallest droplets have coalesced together during normal extrusion without further mixing as the amount of CP has not been enough to stabilize the morphology. Nonetheless, the added CP in the blends with virgin material was able to reduce the size of the PA droplets and this indicates strongly that the CP was able to reduce the interfacial tension by placing to the interface of these phases. This deduction was also supported by the results from the mechanical characterisation.

Altogether, the morphology of the studied compounds presented PE as the continuous matrix phase and PA as a string-like, dispersed phase. The addition of CP in the blend reduced the size of the dispersed droplets, but the adhesion between the phases was rather weak despite the compatibilizer precursor, as even at CP content of 10 wt. % in the matrix the SEM micrographs revealed pulled out PA droplets and voids in the places from which the droplet had separated from the matrix. The compounds containing recycled material, on the other hand, showed strong adhesion between the phases and the sizes of the dispersed PA particles were corresponding to those of observed in the compound PE-B-L15. The compatibilization on the recycled blends did not have any evident effect on the morphology, which could be due to the adhesive component in the recycled blend acting as a compatibilizer precursor or due to the oxidized components reacting with PA and thereby compatibilizing the blend.

5.4 Melt flow properties

The flow properties of the compounds were studied by evaluating the melt flow rate, MFR under a 2.16 kg weight at 230 °C. The temperature of 230 °C was chosen for the test even though the normal MRF temperature for PE is 190 °C because the melting temperature for polyamide was 220 °C and both of the blend components had to be molten so that the MFR could be measured. These results are presented in Table 5.3.

The MFR of PE was only 0.56 g/10 min, which means that it has rather high viscosity, at least at the test conditions. The addition of CP in PE decreased the MFR even more. The MFR of the low viscosity PA was over 40-fold larger than that of PE and even the medium viscosity PA had a MFR of 20-fold larger than PE. As the torque of the studied polyamides was not measured the same type of relations between the flow properties and morphology cannot be drawn as done in the paper of Kudva et al. [19]. They suggested that the large viscosity mismatch, measurements based on the torque, between the blend components in compatibilized blend would lead to a situation in which the minor component with lower viscosity would drive towards being the continuous phase already at volume fractions lower than that of calculated for phase inversion. At the moment only conjectures can be done of the flow properties of the blend components under the processing conditions and therefore the effects of the potential mismatch between the viscosities of the blend components on the blend morphology and thus, on the other properties are unknown.

Table 5.3 MFR values of the compounds

	MFR [g/10min]
PE	0.56
PA-L	23.3
PA-M	10.9
PE-A	0.53
PE-B	0.52
PE-A-L5	0.53
PE-A-L15	0.65
PE-A-M5	0.52
PE-A-M15	0.61
PE-B-L5	0.54
PE-B-L15	0.52
PE-L15	1.14
R100	7.12
PE-R30	0.86
PE-B-R10	0.45
PE-B-R30	0.70
PE-B-R50	1.28

There was no significant difference in MFR between the compounds containing polyamides with differing viscosities, that is, PA-L and PA-M. Even though the compounds with medium viscosity PA showed slightly lower MFR values, the difference is negligible when compared to the difference between the MFR values of the neat PA-L, 23.3 g/10 min and that of PA-M, 10.9 g/10 min. This could be due to the formation of PE-g-PA graft copolymers which affects the MFR more than the possible neat PA phase in the compound or the PE matrix dominating the melt flow properties.

The influence of the PA content on MFR is presented in Figure 5.18. The addition of 15 wt.% of neat PA-L to the neat PE matrix seems to double the MFR of the compound when compared to neat PE. The compatibilization of the virgin blends keeps the MFR values around the values of the matrix materials, although, at 15 wt.% of PA-L the compound with 5% of CP has slightly higher MFR than that of with the PE-B matrix. This is an indication of the formed compatibilizer that bounds the phases together and keeps the PA with better flow properties from affecting the MFR, and of the balancing effect of the formation of the graft copolymer which would normally decrease the flow properties. The same stabilizing effect of the CP was reported by Burgstaller et al. [9].

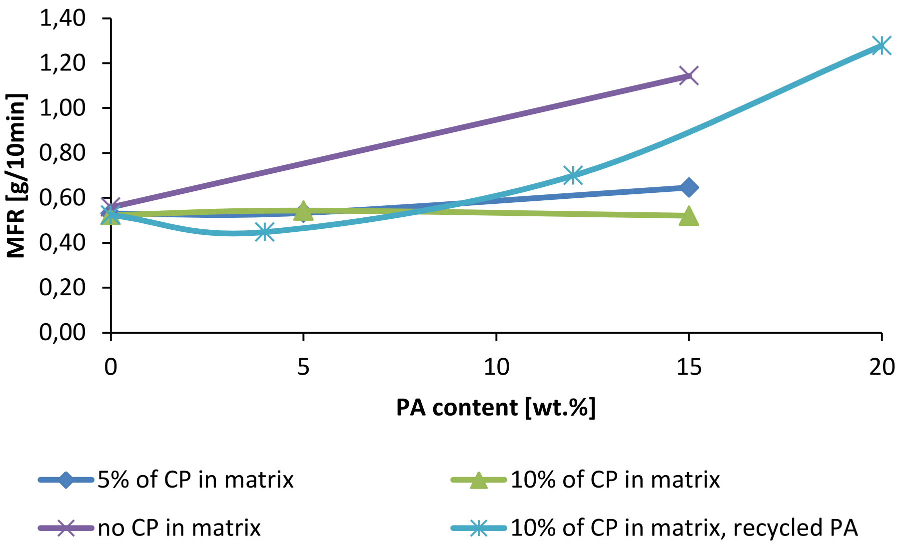


Figure 5.18 MFR as a function of PA content

The compounds containing recycled blends show a slight decrease in MFR when the recycled content is 10 wt.% (approx. 4 wt.% of PA) but starts to increase after that. It can be suggested that the formed graft copolymers decrease the MFR. At recycled content of 30 % the MFR is already higher than that of virgin compounds and 50/50 blend of recycled material and PE-B (approx. 20 wt.% of PA) results in MFR values even higher than that of uncompatibilized 85/15 PE/PA-L blend. The main reason for the prominent difference in the flow properties between the compounds PE-L15 and PE-B-R50 is the high content of recycled material with higher MFR. The recycled blend was identified to contain also LDPE and LLDPE of which melt flow properties we do not have specific information. As R100 had MFR of 7.12 g/10 min it can be assumed that these polymers as the major component have relatively easier melt flow properties than that of the neat PE.

When the MFR of the different compounds containing recycled material are compared the difference between the R100 blend comprising only of the recycled film material and the other compounds is prominent, as seen in Figure 5.19. Even the 50/50 blend PE-B-R50 is only about one fifth of the MFR of R100. This is probably due to the dominance of the PE matrix in the melt flow properties. The uncompatibilized PE-R30 shows slightly higher MFR than the compatibilized PE-B-R30, which indicates the formation of the compatibilizer graft copolymer with the addition of CP in the blend. However, unlike the general trend in all other torque values, the lower MFR does not result here in higher torque, but the addition of CP result also in a smaller torque, which would indicate easier flow properties for the compatibilized blend and, thus, the formation of the compatibilizer would be unlikely.

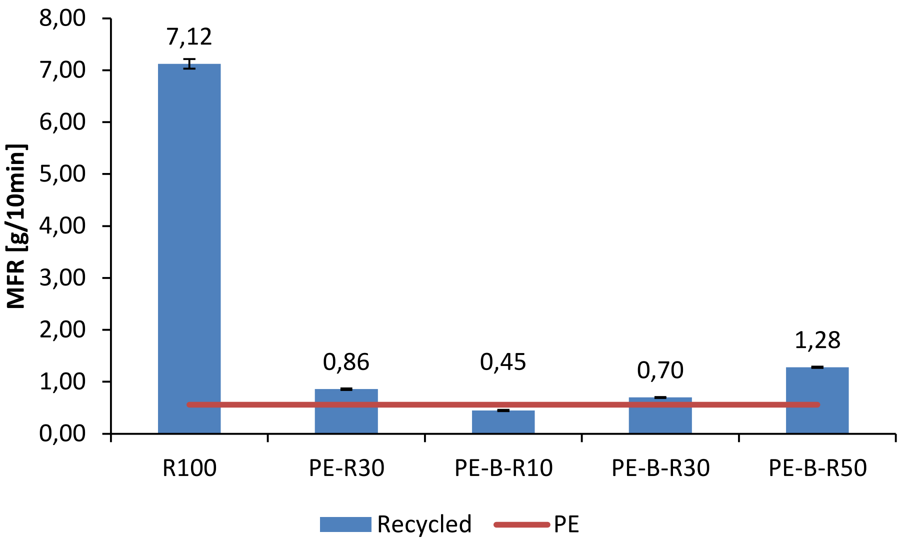


Figure 5.19 MFR of the recycled compounds

Hence, the studied compounds showed rather small differences when using virgin materials and CP, because the formation of PE-g-PA compatibilizer stabilized the melt flow properties when compared to the uncompatibilized blend. The same effect was seen with the recycled material at low recycled content, but as the recycled content increased the other components in the blend affected the MFR by increasing it. The compatibilization of the recycled blend did not have any significant effect on the melt flow properties.

5.5 Thermal analysis

The thermal properties and the melting and crystallization temperatures of the compounds were characterized by DSC. The crystallization temperature, T_c, was analysed from the crystallization peaks at the cooling curve and the melting temperature, T_m, was analysed from the melting peak from the second heating curve. The detected crystallization temperatures and the enthalpy of crystallization, ΔH are collected in Table 5.4. PE and both polyamides showed strong, singular crystallization peaks at the characteristic temperatures, that is, for PE Tc=111.3 °C , PA-L Tc=180.3 °C and PA-M Tc= 182.9 °C. The addition of CP in the PE did not have any effect on the thermal properties of the matrix as the DSC curves for PE-A and PE-B were identical with that of PE.

Table 5.4 Crystallization characteristics of the compounds

Material	Tc_1 [°C]	ΔH_1 [J/g]	Tc_2 [°C]	ΔH_2 [J/g]	Tc_3 [°C]	ΔH_3 [J/g]	Tc_4 [°C]	ΔH_4 [J/g]	Tc_5 [°C]	ΔH_5 [J/g]
PE					111,3	122,1				
PA-L	180,3	71,28								
PA-M	182,9	71,12								
PE-A					111,8	122,5				
PE-B					111,6	121,8				
PE-A-L5			122,3	1,42	111,8	112,0				
PE-A-L15	188,0	0,924	127,1	3,12	111,5	99,7				
PE-A-M5			121,3	0,83	110,9	116,1				
PE-A-M15	188,5	1,35	126,1	2,84	112,1	96,0				
PE-B-L5			120,2	0,43	111,3	119,0				
PE-B-L15			125,6	2,86	111,6	99,9				
PE-L15	189,8	6,13	137,4	1,77	112,6	108,6				
R100	186	12,28			107	20,1	95,6	37,8	60,9	10,9
PE-R30	185,5	2,81			112,1	104,0	x		x	
PE-B-R10	185	x			111,1	111,0			x	
PE-B-R30	185,9	2,78			111,6	98,0	x		x	
PE-B-R50	187	6,05			111,4	88,5	x		x	

x= peak observed

The compounds with virgin polyamide showed fractionated crystallization behaviour, in which the crystallization of the dispersed phase in an immiscible polymer blend has split into two or more crystallization events at lower temperatures. As seen in Figure 5.20 the uncompatibilized blend PE-L15 showed a stronger crystallization peak of the PA phase at Tc_1=189.8 °C with the starting point of the peak at the same temperatures as the crystallization peak of the neat PA-L, and a weaker, delayed melting peak at 137.4 °C. The addition of CP in the 85/15 PE/PA blend is shown in Figure 5.20 as the delayed peak shifts towards lower temperatures and the characteristic PA crystallization peak at 189 °C weakens or even disappears completely. As evident in Table 5.4 the shift of the delayed peak is even stronger for example in the blend PE-B-L5 in which the CP/PA ratio is the highest of all the compounds. This evolution of the delayed crystallization peak is an indication of efficient compatibilization, as stated by Yordanov and Minkova [32]. According to the results, the higher the CP/PA ratio is the stronger the shift of the delayed crystallization peak is and therefore it can be suggested that the degree of compatibilization increases by the increasing CP/PA ratio. The crystallization peak for PE phase remained rather unaffected by the addition of PA in the blend.

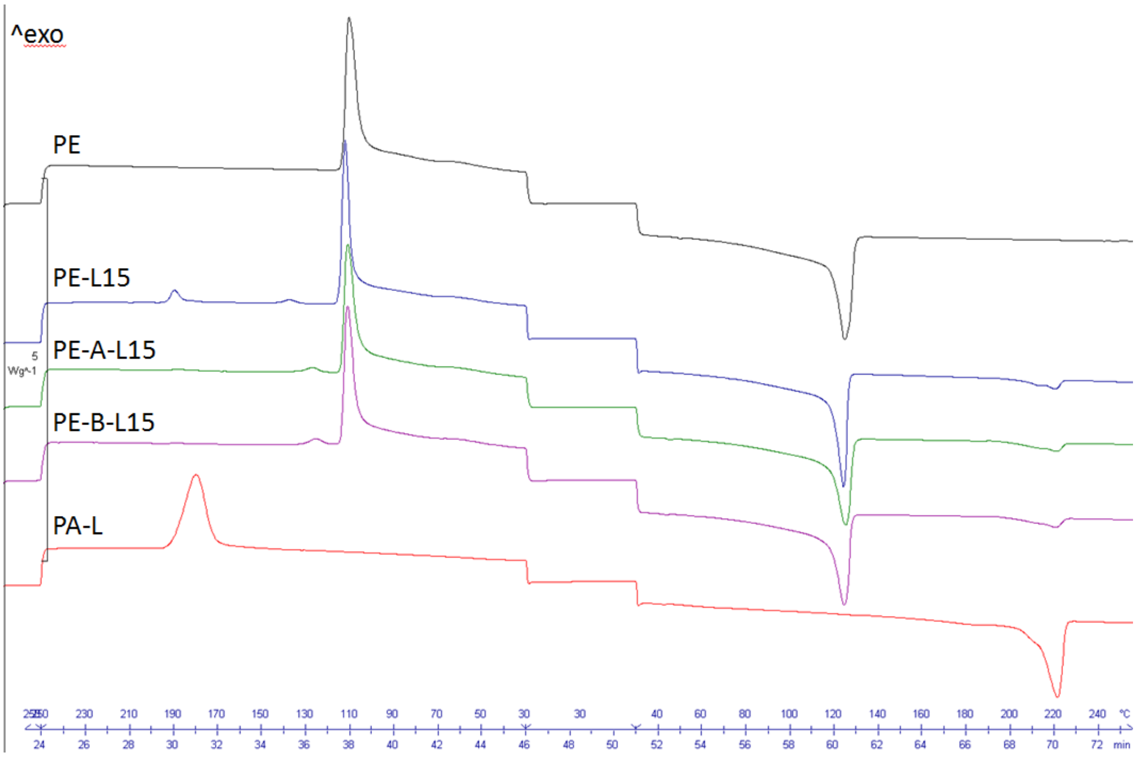


Figure 5.20 DSC curves, 1st cooling and 2nd heating

Table 5.5 presents the characteristics for the phase transition of melting. Also the crystallinity of the PE phase is presented in this table. The melting peaks of the compounds containing only virgin polymers were unaffected by the changes in the blend composition or by the compatibilization. The melting peaks for the PE phase were observed around 124 °C and for the PA phase around 220 °C.

The DSC curve of R100 showed multiple crystallization and melting peaks representing the different components in the recycled blend. At least the melting peaks for LDPE, LLDPE and PA were identified at 108, 120 and 219 °C, respectively. The compounding with PE or PE-B matrices weakened the melting and crystallization peaks of the other substances and added the melting and crystallization peaks characteristic to PE to the DSC curves. As reported also in the context of other studied properties, no difference was obtained between the uncompatibilized and compatibilized blends with 30 wt.% of recycled material, but the DSC curves of PE-R30 and PE-B-R30 were identical. Because the fractionated crystallization of the dispersed phase in an immiscible polymer blend has been related to the small enough particle size, limited by a certain critical diameter, of the dispersed phase [32] it is surprising that no fractionation of the crystallization peak is evident in the blends with recycled material, even though the morphological analysis revealed the particle size of for example the PE-R30 blend to be at least as small as in PE-B-L15 with strongly fractionated crystallization. The crystallization peak of the PA phase in the recycled blends changes only by the size of the peak, which is evident in the enthalpies of crystallization listed in Table 5.4. The lack of fractionation despite the fine morphology of the dispersed PA phase could have something to do with the additives and other substances in the recycled material which could somehow hinder the delaying of the crystallization.

Table 5.5 Melting characteristics of the compounds

Material	T_{m1} [°C]	ΔH_1 [J/g]	T_{m2} [°C]	ΔH_2 [J/g]	T_{m3} [°C]	ΔH_3 [J/g]	PE Crystallinity [%]
PE			123.7				43,9
PA-L					220.9	-81.93	
PA-M					220.8	-77.17	
PE-A			123.8				43.97
PE-B			123.6				43.6
PE-A-L5			123.8		219.4	-3.57	40.29
PE-A-L15			124.8		220.7	-9.93	35.94
PE-A-M5			125.2		220.7	-3.71	40.43
PE-A-M15			124.2		220.3	-9.92	36.24
PE-B-L5			124.0		219.5	-3.20	42.9
PE-B-L15			124.0		220.2	-10.6	36.21
PE-L15			123.8		220.2	-8.88	36.54
R100	108.8	-53.0	119.7	-13,7	218.3	-10.6	
PE-R30	x		123.5		218.5	-3.21	37.68
PE-B-R10	x		124.3		218.4	-1.31	39.76
PE-B-R30	x		123		218	-3.70	35.69
PE-B-R50	x		122.6		218	-5.84	32.11

x= peak observed

In general, the PE and PA phases in the blends showed clear separate melting and crystallization processes by having separate peaks for each phases. The blends with virgin materials showed fractionated crystallization and the addition of CP shifted the delayed crystallization peak to lower temperatures. The higher the CP/PA ratio was the stronger the shift was. This shift can be taken as an indication of an effective compatibilization. In the compounds with recycled material no fractionated crystallization was observed despite the small particles observed in the morphological analysis. The unknown additives and other substances or the oxidised components in the recycled blend could have affected the crystallization of the PA phase in the recycled blends.

6. CONCLUSIONS

Two sets of reactively compatibilized compounds with variety of blend composition were studied. The matrix material in all compounds was a commercial Borstar® polyethylene and depending on the compound 5 or 10 wt.% of maleic anhydride grafted compatibilizer precursor, CP was added to the matrices. The minor phase in the first set of compounds was low viscosity or medium viscosity polyamide 6 or a blend of recycled packaging film material comprising at least of polyamide and polyethylene. The effects of the blend composition and the CP content in the matrix were studied by mechanical tests of tensile properties and Charpy impact strength and by morphological, melt flow rate and DSC thermal analysis. The objective of the thesis was to evaluate the behaviour of the Borstar® polyethylene, PE as a matrix material for neat polyamide with different viscosity and for the recycled material when the blends are reactively compatibilized by using a maleic anhydride grafted polyethylene as CP.

The most significant finding was that the commercial PE-g-MA compatibilizer precursor used in the study showed a strong compatibilizing efficiency towards the virgin blends of PE and polyamides with low and medium viscosities. The CP did not have any significant effects on the properties of the pure matrix material.

The mechanical properties of the compounds were good indicators of the interfacial adhesion between the blend components as they describe the ability of the stress distribution under different type of mechanical stresses and impacts. The Charpy impact strength of 85/15 PE/PA-L blend was increased by 250 % with the addition of 5 wt.% of CP in the matrix, and by almost 480 % with 10 wt.% of CP. The latter blend resulted in impact strength approximately 10 % higher than those of PE or PA which demonstrates well the toughening effect of the dispersed PA droplets in the matrix and the good adhesion between the phases. The tensile moduli of the compounds were slightly affected by the compatibilization as the addition of CP decreased the modulus. The effect was seen also in the strain at break observed in a tensile tests for 85/15 PE/PA blend as the addition of CP in the blend increased the strain from 10 to over 400 %.

As expected, the addition of CP in the PE/PA blend affected the blend morphology by decreasing the size of the dispersed phase droplets. This was due to the reduced interfacial tension between the phases as the in-situ formed PE-g-MA compatibilizer locates to the interfaces. The effect of the compatibilization on flow properties was observed in the decreased MFR as the MFR of the uncompatibilized 85/15 PE/PA blend decreased approximately 65 % when 10 wt.% of CP was added to the matrix phase. The MFR of the compatibilized blend was even smaller than that of the neat PE, which indicates strongly of the formation of grafted structures in the compatibilized blend.

The thermal analysis conducted by differential scanning calorimetry, DSC revealed fractionated crystallization in the PA phase for blends with virgin components. The higher the CP/PA ratio was the stronger the shift of the delayed crystallization peak to lower temperatures was which can be taken as an indication of increasing compatibilization efficiency.

The compatibilization efficiency of the PE-g-MA compatibilizer precursor in the blends of PE and recycled packaging material blend showed no evidence. The differences in all the studied properties; visual, thermal, morphological, melt flow or mechanical were negligible between the uncompatibilized and compatibilized blends comprising of 70 wt.% of PE and 30 wt.% of recycled material.

Despite the lack of the evidence of working CP the Borstar® polyethylene demonstrated a good behaviour as the matrix material for the recycled blend. The observed morphology for 70/30 PE/recycled material blend showed small, evenly distributed PA droplets in PE matrix with good adhesion between the phases. The sizes of the dispersed droplets were approximately the same range as observed in the virgin blend with 15 wt.% of PA and 10 wt.% of CP in the matrix. Despite the small sizes of the dispersed particles, no fractionated crystallization was observed in the DSC scans.

When the properties of the blends with the recycled component were analysed based on the calculated polyamide content and compared to the trends observed in the virgin blends only in the strain at yield the recycled blend is observed to increase as the virgin blends decrease. All the other analysed quantitative values for the recycled blends showed the same increasing or decreasing trends as the virgin blends.

The reason for the differing behaviour of the recycled blends when compared to virgin blends and possibly for the inefficient compatibilization with the CP is probably in the other content of the recycled blend than the PA phase, which the experimental part was focused on. It was analysed that the recycled blend contained at least PA, LDPE, LLDPE and possibly some sort of an adhesive material used to tie the PE and PA layers together in the packaging films. It is possible that this adhesive material acts as a CP itself and thus no additional CP is needed in the blends of PE matrix and recycled multilayer packaging film material. Another reason for the fine morphology and the lack of difference between the compatibilized and uncompatibilized recycled blends could be in the oxidized substances in the recycled blend originating from the additional processing steps the recycled blends was subjected to, indicated by the darkened colour of the recycled compounds. These oxidized polar groups could also react with PA and thereby compatibilize the blend.

Possible further actions to conduct would be to perform a comparative analysis in which a different type of matrix with, for example, lower viscosity or unimodal structure is used. Also a more detailed analysis on the content of the recycled blend would be necessary to understand the reactions occurring during compounding. The identification of the possible applications in which a blend with recycled content in it could work is important. This would give more specific frames for the research conducted and it would help to direct the resulting properties in the right direction, if modification of the blend composition is an option.

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APPENDIX A: COMPOUNDING PARAMETERS

	Compound	Screw speed [rpm]	T melt [°C]	P melt [bar]	Torque [%]	Productivity [kg/h]
Matrix blends	PE-A	200	206	27-29	89-92	9
	PE-B	200	207	27-29	84-86	9
Experimental blends	PE-L15	200	263	10	56-57	9
	PE-A-L5	200	246	20-21	69-71	9
	PE-A-L15	200	245	19-20	64-66	9
	PE-A-M5	200	244	17-19	70-72	9
	PE-A-M15	200	245	13-14	54-55	7
	PE-B-L5	200	243	16	62-63	8
	PE-B-L15	200	243	16-17	63-65	8
Recycled blends	R100	200	241	2	43	2.5-3
	PE-R30	150	243	5-7	53-55	5
	PE-B-R10	150	244	8-9	54-55	5
	PE-B-R30	150	243	6-7	49-50	5
	PE-B-R50	150	243	4	42-43	5

APPENDIX B: COMPARISON OF THE TENSILE PROPERTIES OF THE COMPOUNDS WITH PA-L AND PA-M

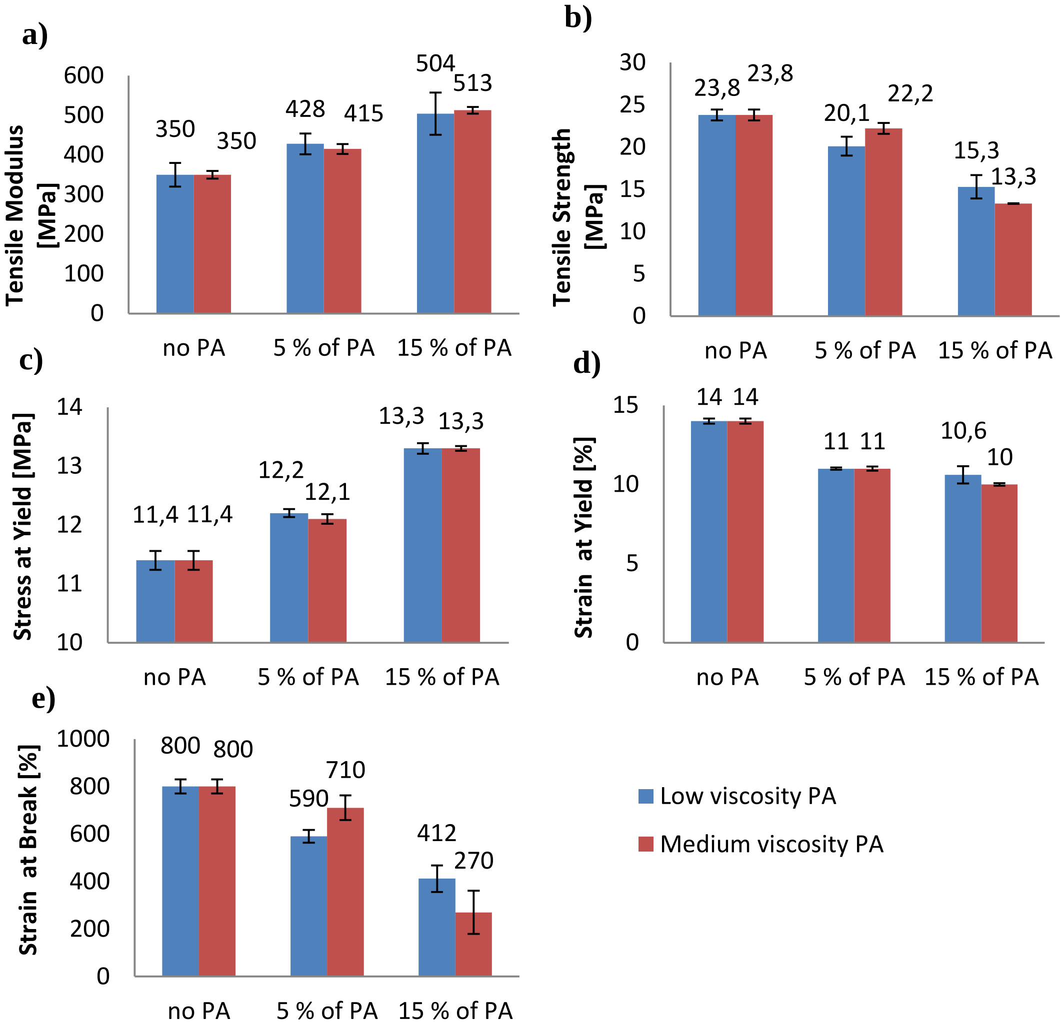

Figure 6.1 Tensile properties of the compounds containing 5 wt.% of CP and low viscosity PA or medium viscosity PA (a) Tensile Modulus, (b) Tensile Strength, (c) Stress at Yield, (d) Strain at yield and (e) Strain at Break

APPENDIX C: SEM MICROGRAPHS OF DISPERSED FIBROUS POLYAMIDE DROPLETS

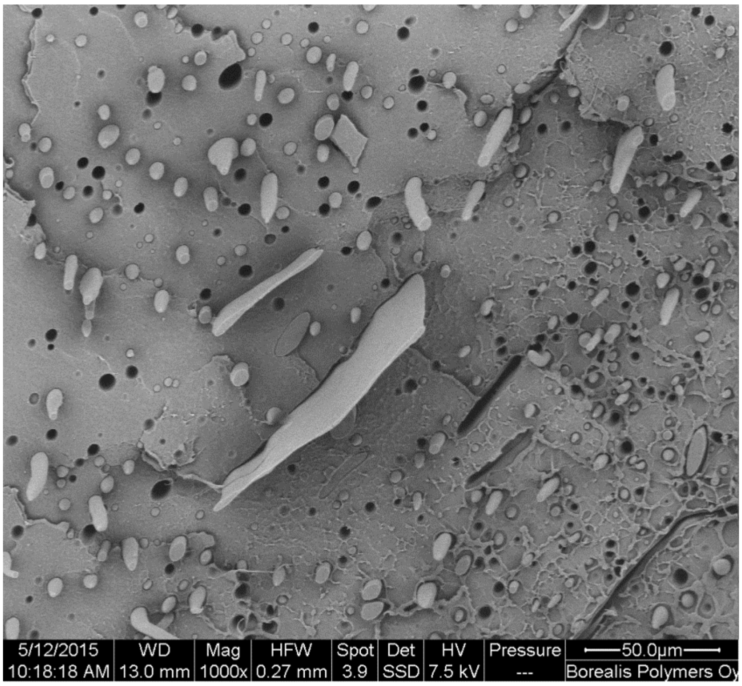

Figure 6.2 PE-L15

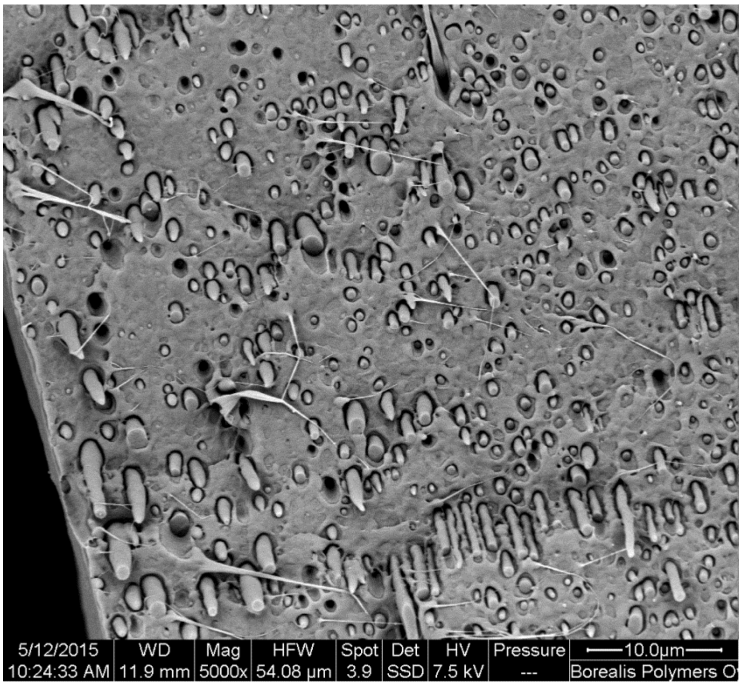

Figure 6.3 PE-A-L15

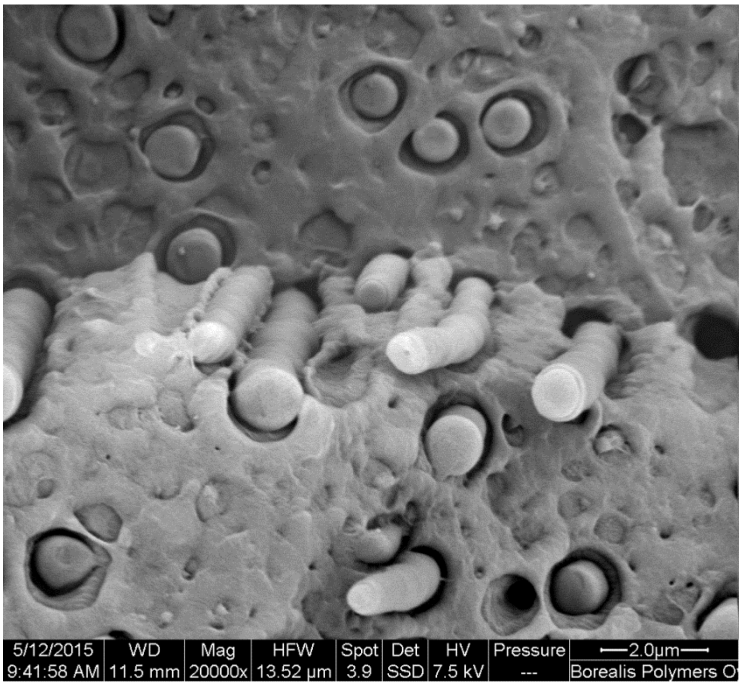

Figure 6.4 PE-B-L15

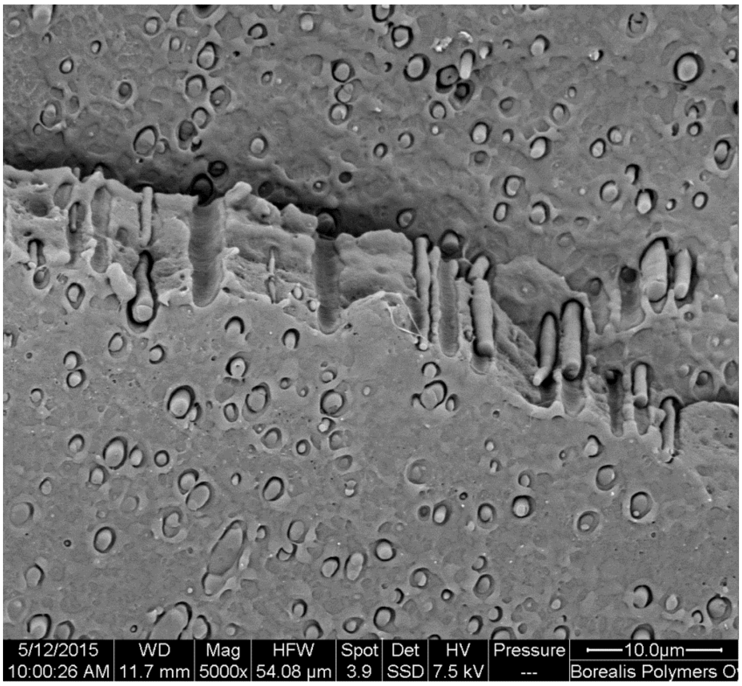

Figure 6.5 PE-B-R30