

Model system study of recycled polyethylene terephthalate and polypropylene blends

by

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Cover: Left: Microstructure of a PP/PET blend with 70/30 wt% ratio and without additives. Right: Microstructure of a PP/PET blend with 70/30 wt% ratio and addition of 3 wt% compatibilizer Epolene G 3015.

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Abstract

Recycling of polymers becomes an increasingly important issue because of the environmental impact of petroleum-based polymer production. Legislative motivation also pushes for polymer recycling with the End-of-Life-Vehicles (ELV) directive dictated by the European Union requiring that a minimum of 85 wt% of vehicles are materials recycled. This creates a need to recycle interior parts from cars for example compression molded panels that consist of several polymers, such as polypropylene (PP) and polyethylene terephthalate (PET).

Recycling of polymer blends can be a problematic process due to phase incompatibility. The compatibility of PP and PET, can be increased by adding compatibilizing agents that lower the interfacial tension. Adhesion between the phases can be increased as well resulting in a stronger and more elastic material. During processing of PET, degradation by hydrolysis results in loss in molecular weight. Chain extenders can be added to counteract this effect and thereby strengthening the material.

The aim of the master's thesis work was to investigate a system model for processing and upgrading recycled PP and PET fibers that can be industrially applicable. This was done by evaluating virgin PP pellets and PET fiber blends. The upgrading was performed by adding compatibilizing agents and chain extenders to the PP and PET blends. The study focused on maximizing the mechanical properties for the blends produced. The effect of compatibilizers, chain extenders and glass fiber was analyzed with mechanical analysis, differential scanning calorimetry, fourier transform infrared spectroscopy and scanning electron microscopy.

The results showed that for maleic anhydride grafted PP compatibilized blends the yield strength was increased and combined with epoxy or oxazoline chain extenders even higher yield strength was observed. This was achieved by a very good dispersion of PET the phase in the PP matrix. High shear mixing in a regular twin screw extruder showed that the concept is industrially applicable.

Keywords: recycling, polyethylene terephthalate, PET, polypropylene, PP, compatibility, chain extension, maleic anhydride, glycidyl methacrylate, oxazoline.

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Introduction

Compression molded textiles are used substantially in the automotive industry in the form of interior panels and sound absorbers. These components are found mainly in the coupe and in the trunk of cars. The textile material consists of combed fibers commonly constituted of both polypropylene and polyethylene terephthalate with a backing of PP. The End-of-Life-Vehicles (ELV) directive dictated by the European Union require as of January 2015 that a minimum of 95 wt% of vehicles are recycled, of which 85 wt% should be material recycling. This creates an incentive to recycle the compression molded textile components into polymeric material with attractive properties.

Polymer recycling is a process that includes disassembly, sorting and grinding of the raw materials followed by upgrading through compounding with additives and granulation. The granules can be used for the consumer goods production, produced by for example injection molding. When recycling polymer components from cars a large number of different polymers will be collected. Many compressive molded panels are made of PP/PET with approximately a 50/50 wt% ratio. Rigid backings are often made of injection molded PP. Therefore, recycling of these materials can give a variable range of the polymer composition. A PP/PET ratio of 70/30 wt% was chosen for the model system in this study. The choice was made in order to ensure that PP will constitute the matrix and PET will be present in amounts that can influence the material properties. If positive results for this system are obtained they should be applicable to blends with less PET as well. This means that the results from the study can be applied for a wide range of PP/PET blends that can be of interest in the recycling of PP and PET waste.

A model system investigation with virgin PP and PET enables a controlled study of the PP and PET recycling and upgrading process. The known composition and absence of contaminants in the virgin material give fewer variables that otherwise can lead to misinterpretation of results.

Pure PP and PET mixtures exhibit poor compatibility due to large interfacial tension which limits the mechanical properties of such blends. In order to make PP and PET compatible, compatibilizing agents can be added to reduce the interfacial tension and increase the adhesion between the two phases. Examples of effective PP/PET compatibilizing agents should therefore have one segment with affinity to PP and another to PET. PP grafted with functional groups with either affinity for the PET phase or capability to react with PET's end groups has been investigated

in recent research with positive results.

During recycling of PP and PET blends by reactive extrusion and injection molding degradation of the polymers inevitably occurs. The degradation is especially prominent in PET which undergoes hydrolysis even in the presence of trace amounts of water. The twin-screw extruder used in this study is equipped with a vacuum degassing system to remove volatiles such as water. Because of the high temperatures needed to melt and process PET, degradation, and therefore loss of molecular weight, will occur. Chain extenders, which can react with PET end groups and create longer chains or cross link molecules, can be used to counterbalance the degradation. By chain extending the PET phase the processing of the polymeric blend can be eased significantly and the mechanical properties of the materials produced can be improved.

The compatibilizing agents and chain extenders used need to be commercially available bulk chemicals and thermally stable. Characterization of the mechanical properties is central in this study, since the mechanical properties determine the possible use of the produced blends, but chemical, thermal and microscopic analysis are used to understand and explain the mechanical results. The results from the project will be essential input for industrial scale recycling of PP/PET blends from manufacturing waste, post-consumer compression molded textiles and other sources.

1.1 Aim

The aim of the master's thesis work was to investigate a model system for processing and upgrading recycled PP and PET fibers that can be industrially applicable. This was done by evaluating virgin PP pellets and PET fiber blends. The upgrading was performed by adding compatibilizing agents and chain extenders to the PP and PET blends. The additives need to be commercially available, thermally stable and nontoxic. Processing parameters and component compositions were optimized with the aim to maximize the mechanical strength

2

Theory

2.1 Polyethylene terephthalate

Polyethylene terephthalate (PET) is a thermoplastic polyester with the ethylene terephthalate repetitive unit (Fig. 2.1). It constitutes a significant portion of the global plastics consumption and is mainly used for textiles and packaging [1]. PET is produced by the polycondensation method in a two stage process. First either ethylene glycol and terephthalic acid undergo esterification or a transesterification of ethylene glycol and dimethyl terephthalate is performed. This produces the product bis(2-hydroxyethyl) terephthalate. To propel the reaction forward, water is removed in the first case and in the latter methanol is removed. Bis(2-hydroxyethyl) terephthalate is then polymerized into PET by polycondensation whilst removing water continuously [2].

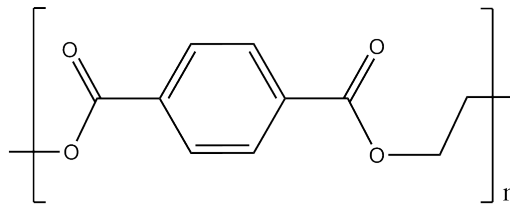


Figure 2.1: Structural composition of polyethylene terephthalate.

Due to the polarity of the ester segments, PET is a hygroscopic polymer and will adsorb up to 0,8 wt% water at room temperature depending on the relative humidity [3]. Therefore, in order to avoid hydrolysis, drying is necessary before processing at elevated temperatures. Depending on the processing history, PET can exist as either an amorphous or a semi crystalline polymer. The degree of crystallinity also affects the hygroscopicity of PET because water can only diffuse to an ester site positioned in the amorphous regions [4].

2.1.1 Degradation

During mechanical recycling processing of PET extensive degradation may occur. The main reactions associated with the degradation of PET in the mechanical processing are hydrolysis and acidolysis and thermal degradation. Similar for all reactions are different forms of chain scissions with a resulting drop in molecular weight of the PET which lowers the viscosity and thus its processability. Upon degradation

into shorter polymer chains, the crystallinity increases and therefore also higher glass transition temperature and melting temperature. Also the degrading reactions have in common that they primarily occur at the ester bond which is the weakest bond in the PET chain [5]. To constrain overall degradation, processing temperature should be kept as low as possible yet keeping PET in molten state.

2.1.1.1 Hydrolysis

PET undergoes hydrolytic degradation at elevated temperatures in the presence of water (Fig. 2.2). The reaction is initiated by a carbocation formation on the ester segment followed by a nucleophilic attack of a water molecule. The resulting chain scission creates a carboxylic end group and a hydroxyl end group. A temperature of at least 260 °C is needed during the processing of PET to ensure that all of the PET is in melt. At this temperature, the hydrolysis reaction readily uses up all of the water molecules present in the polymer melt [6]. Hydrolysis is the dominating degradation reaction and has a reaction rate several orders of magnitude higher than that of thermal oxidation [7].

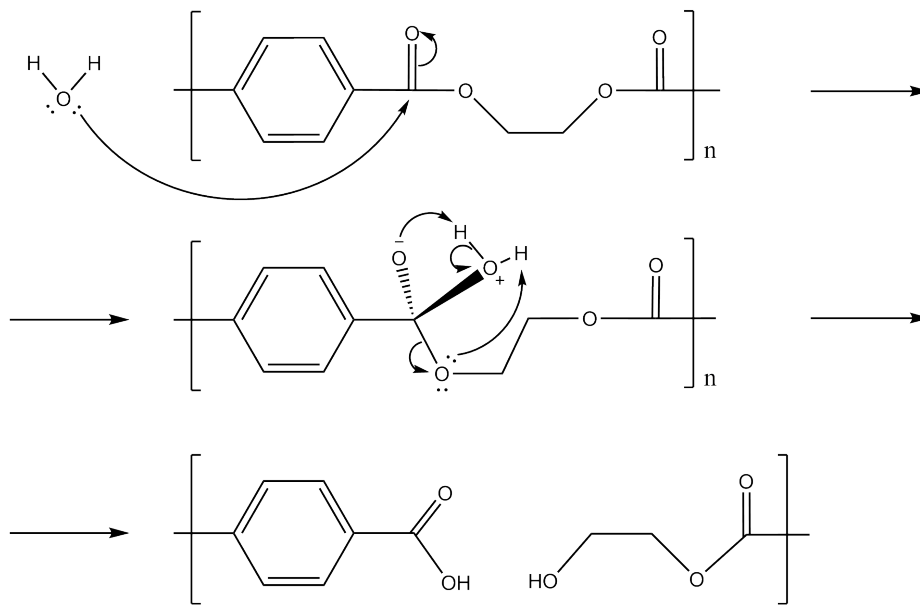


Figure 2.2: Mechanism for the hydrolysis of PET

In order to avoid the hydrolysis reaction with a resulting loss of molecular weight, the water content in the polymer should be below 0,02 wt% which can be obtained by drying the PET in dehumidified air at temperatures above 120°C before processing [8]. Another way to repress hydrolytic degradation is by removing the water vapor formed in the extrusion and injection molding stages by vacuum.

2.1.1.2 Thermal degradation

The thermal degradation of PET is a random chain scission mechanism initiated by a cleavage of the alkyl oxygen bond resulting in a carboxyl end group and a vinyl

ester end group (Fig. 2.3) [9, 6]. The carbon-carbon bond is thermodynamically weaker than the carbon-oxygen bond but upon rupture of the latter, resonance stabilized radicals are created.

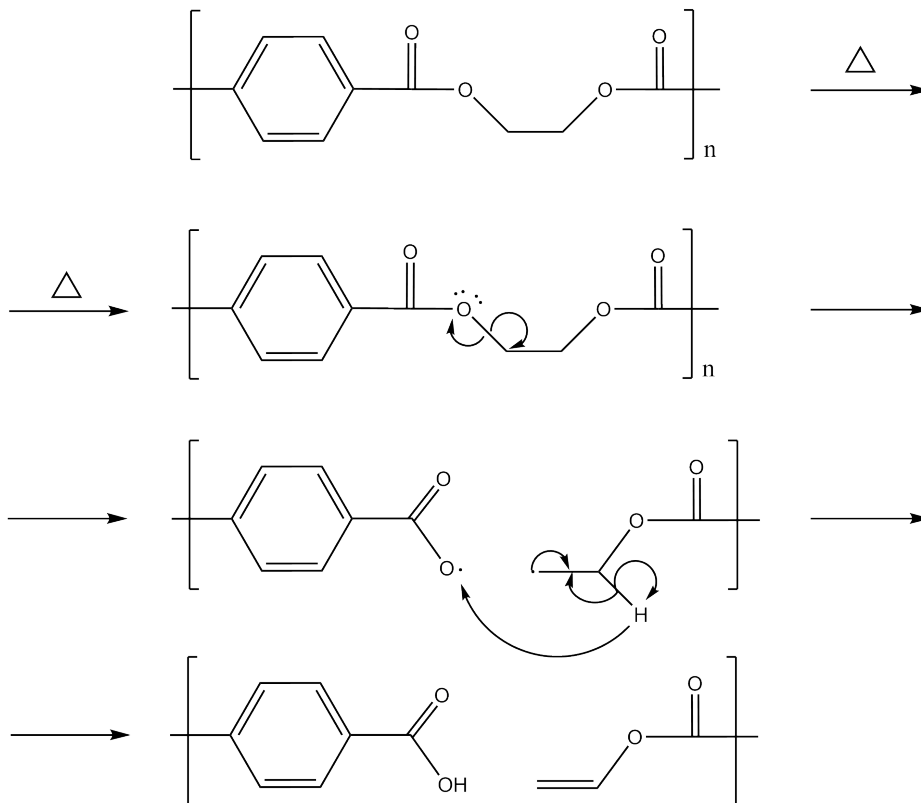


Figure 2.3: Mechanism for the thermal degradation of PET.

The propagation of the decomposition mechanism involves formation of cyclic and linear oligomeric compounds where the latter primarily forms hydroxyl end groups [8, 10]. Further decomposition results in thermodynamically stable gaseous compounds such as acetaldehyde, water, carbon monoxide and carbon dioxide [10]. The acetaldehyde formation is a result of reaction between a vinyl ester end group and an hydroxyl end group, followed by elimination of acetaldehyde leaving an anhydride segment in the polymer [11]. In the presence of oxygen, the thermal degradation can be accelerated via hydroperoxide formation on the methylene bridge of PET.

2.2 Polypropylene

Polypropylene (PP) is a thermoplastic polyolefin of the propylene monomer (Fig. 2.4). The methyl group attached to the polymer backbone can be arranged different along the polymer backbone, creating three different configurations; isotactic, with all the methyl groups pointing the same way, syndiotactic, with methyl groups pointing in alternating direction and atactic, without long range order of the methyl

groups. The configurations formed is controlled by the choice of heterogenous catalyst. The properties of polypropylene is influenced by its stereochemistry. The degree of regularity thus gives isotactic polypropylene the highest crystallinity. A variety of properties can be tailored by modifying tacticity and molecular weight to create a purpose specific polypropylene. Polypropylene, like other polyolefins, is highly hydrophobic and does not demonstrate hygroscopic behavior [12].

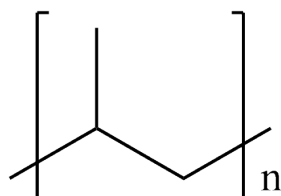


Figure 2.4: Structural composition of PP

2.2.1 Degradation

Polypropylene is primarily degraded by thermal degradation. The mechanism follows the random chain scission mechanism and is initiated by a radical alkyl and resulting in fragmentation at the tertiary carbon of PP which is the most stable radical site [13]. The fragmentation of the radical tertiary carbon follows the beta scission mechanism where the tertiary radical is split into a radical alkyl and an alkene (Fig. 2.5). Thermal degradation is accelerated in the presence of oxygen and oxidative thermal degradation is observed starting at 150 °C and is accelerated with increasing temperature [14].

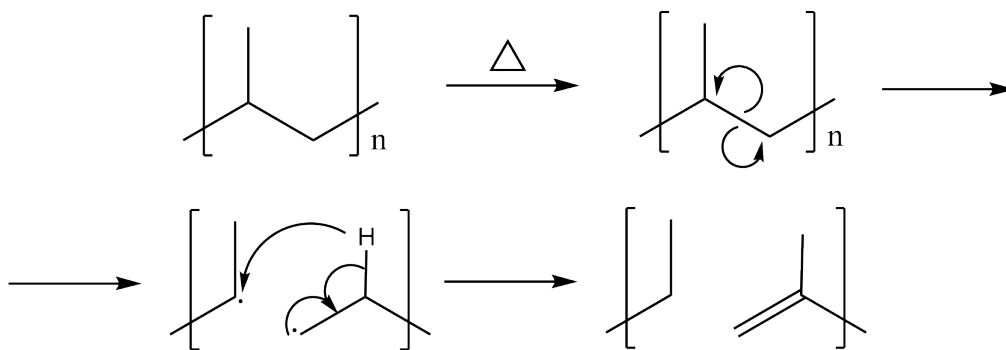


Figure 2.5: Mechanism of the thermal degradation of PP

2.3 Compatibilization

Blends with polar and non-polar polymers characteristically exhibit poor compatibility through high degree of phase separation, which results in inferior processability and mechanical properties. The miscibility of different polymers is ruled by thermodynamics and can be modified by incorporation of compatibilizing agents that

lower the interfacial tension of the system. A typical polymer-polymer compatibilizer consists of segments with high affinity for respective polymer phase. Polymers that are exposed to high degree of degradation during processing, such as PET, can be recovered by chain extenders, a group of compounds that increase the molecular weight of the polymers by chain extending or cross linking.

2.3.1 Miscibility

Polymer miscibility is determined by solubility thermodynamics and will occur with negative free energy of mixing but can also be expressed in terms of interfacial tension between the polymer phases [15]. In between full miscibility and complete phase separation there is a dynamic range of degrees of miscibility. Complete miscibility of different polymers is unlikely due to the low contribution to entropy when mixing [16]. However, attractive mechanical properties can be obtained by high interfacial adhesion of the polymer blend so that externally applied stresses and strain can be distributed through the matrix efficiently [1]. Depending on which component that is highest in content, and thus constitutes the matrix, the properties of the blend can differ greatly. Ronkey et. al. determined that PP was the matrix material in PP/PET blends with a PP/PET wt% ratio of 60/40 or more PP. Also, during processing of polymer blends, the time at high temperature is often minimized in order to avoid degradation reactions. Therefore, in order to achieve adequate dispersion of phases in a short time a high degree of mixing is needed during blend processing. Due to the thermodynamic instability of poorly miscible polymer blends post-process temperature treatments, such as annealing, can greatly influence morphology [1].

The poor miscibility of PP and PET can be explained by the difference in their chemical composition. PET is a polar polymer and has relatively strong dipole-dipole interaction forces, also known as Keesom forces, between the polymer chains. The cohesiveness of the non-polar PP on the other hand is due to weaker London dispersion forces. The interaction between PP and PET will be therefore be a result of dipole-induced dipole interactions, also known as Debye forces, but these are several orders of magnitude weaker than the dipole-dipole interaction forces of PET [17]. The energy of a blend will thus be minimized if the interaction between the two phases is limited.

2.3.2 Compatibilizers

The issue of poor miscibility of polymer-polymer blends can be dealt with by addition of compatibilizing agents with high interphase affinity that reduce the interfacial energy. The objective for compatibilizing blends is to create commercially useful polymer blends that, on the molecular scale, achieve a thermodynamically stable low degree of phase separation [18]. With increase in compatibilizing agent content and thus decreased interfacial tension, the degree of dispersion increases giving smaller droplets of the dispersed phase [16, 1].

Block or graft copolymers are commonly used compatibilizing agents but compatibilization can also be achieved by creating bonds between the different polymers in the blend using in situ chemical reactions [1]. Block copolymers, 2.6a, composed of segments with high or complete affinity for respective blend component are ideal compatibilizing agents but are seldom available commercially. Graft copolymers, figure 2.6b, are polymer chains chemically equivalent with one of the blend components but with grafted groups that either has high affinity or reactivity with the other blend component. Compatibilization requires that the compatibilizer finds the interface, but the diffusion of high molecular weight copolymers in a high molecular weight polymer blend is very limited. Therefore thorough mixing is essential for good compatibilizer interface distribution [1].

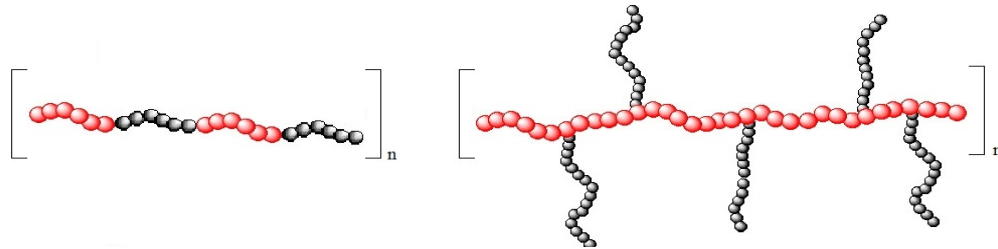


Figure 2.6: Structural composition of a) block copolymer and b) graft copolymer.

For PP and PET blends a wide variety of compatibilizing agents have been investigated in recent years [19, 20, 21, 22, 23, 24, 25, 26]. The studies investigate compatibilization by grafting of various polyolefins with different groups that are known to either interact with the polar segments of PET or by means of reaction with the end groups of PET. The most effective compatibilizers unanimously reported are PP grafted with either maleic anhydride, MA, or glycidyl methacrylate, GMA. The PP segments in such compatibilizers can entangle in the PP phase and the reactive GMA or MA groups interact or react with the PET phase. Abdul Razak et. al. investigated PET/PP 70/30 blends and obtained an increase in the tensile strength from 37 MPa to 42 MPa, a 13,5 % increase, with MA-compatibilizer [19]. Khonakdar et. al., investigated PET/PP 75/25 blends and reported increasing viscosity with a GMA-compatibilizer and decreasing viscosity for a MA-compatibilizer. This was explained by the stronger interaction for the epoxy compound in the GMA with the PET phase [20]. Asgari and Masoomi, who investigated PP/PET-fiber composites, reported an increase in tensile strength from 30 MPa to 33 MPa, a 10 % increase, with PP-g-GMA compatibilizer and from 30 MPa to 31 MPa with PP-g-MA compatibilizer [23]. Both MA and GMA have selective reactivity for the respective end groups of PET, where maleic anhydride reacts to a larger extent with the hydroxyl end groups and glycidyl methacrylate has higher reactivity with the carboxyl end groups [9, 27].

2.4 Chain extension

Chain extenders are chemical compounds with a functionality of two or more, and thereby with the ability to chain extend or to cross-link polymer chains. The objective of such additives is to increase the molecular weight of polymers that are prone to degradation reactions during processing. Chain extenders can be classified in terms of functionality, which describes the number of reactive sites on each molecule. Chain extenders can range from low molecular weight compounds with limited functionality to high molecular weight multifunctional compounds. A variety of functional groups have been investigated on their chain extending ability on the end groups of PET, including; hydroxyl, epoxy, carboxyl, anhydride, oxazoline, cyanide and amine - compounds [5]. The functional groups undergo different reaction mechanisms that differ in reactivity, and especially in the selective reactivity towards hydroxyl and carboxylic end groups of PET as well as the bond stability after reaction [28].

When chain extenders are added in polymer blends it is important that the chain extender has selective affinity for the phase in which the reaction is intended in order for chain extender to encounter the reactive site. For PP and PET blends where PET is predispositioned to a higher extent of degradation, a chain extender with polar and aromatic segments will have higher affinity for the PET phase than for the polyolefinic PP phase [9]. As an alternative to low molecular weight chain extenders, tailor made oligomeric chain extenders with high functionality and high reactive phase affinity contribute with both linear and cross-linking chain extension [29]. The processing window for chain extenders with a high degree of functionality is limited due to the possibility of high network formation even at low chain extender concentrations resulting in a polymer gel with high or infinite viscosity. However, this issue can be addressed by distributing the chain extending functional groups along the oligomeric chain [30].

The maximum concentration chain extender added must be taken into consideration so that the extrusion system remains operational [9]. If the degree of reticulation reaches a continuous three-dimensional network the polymer blend forms a gel with hindered processability. For all types of chain extenders, the risk of high degree of network formation is a factor.

2.4.1 Characterization of chain extension

There are a number of techniques available to analyse the degree of chain extension after reaction in a polymer melt. Intrinsic viscosity, IV, and melt flow index, MFI, are used for chain extension characterization and are important processing parameters. IV is measured with a Ubbelohde tube and MFI is measured by MFI measuring equipment. Chain extension reaction can be indicated by studying the changes in IV and MFI because longer chains should theoretically give a higher IV and lower MFI [28, 27, 31].

PET chain extension can be chemically analysed by infrared spectroscopy, carboxyl-concentration and molecular weight distribution. Studying the changes in absorption peaks from infrared spectroscopy is a widely used method including chain extension determination [32, 33]. PET chain extension is based on the reaction with PET end groups and the end group concentration changes can be measured by pH titration [27]. The molecular weight of processed PET is decreased due to degradation and adding chain extenders have the potential to balance this drop or even increase the molecular weight compared . Thus by studying the molecular weight distribution the chain extending reaction can be determined [28, 27]. Molecular weight distribution is commonly determined by gel permeation chromatography.

2.4.2 Epoxy chain extenders

The effectiveness of chain extension of PET with epoxide reactions has been proven and investigated further in recent years and included regular epoxides, glycidyl ethers and glycidyl methacrylate, where the latter has shown highest reactivity with PET [28, 27, 29]. The epoxide group can react upon nucleophilic attacks from both carboxyl end groups and hydroxyl end groups of PET, but the reaction rate of carboxyl end group reaction is dominant. The mechanism for the carboxyl-epoxide reaction follows the epoxide ring-opening mechanism shown in Figure 2.7, where the nucleophilic carboxylic acid reacts with either of the electrophilic carbon [34]. Reaction at the tertiary carbon is the thermodynamically most preferable site since it gives the most stable carbocation intermediate, but the secondary carbon is less sterically hindered. The difference in the final product however is of negligible importance. The residual epoxide oxygen is converted into either a primary or a secondary hydroxyl which gives the possibility for further reaction with either a carboxylic acid or an epoxide which will result in branching of the polymer [32].

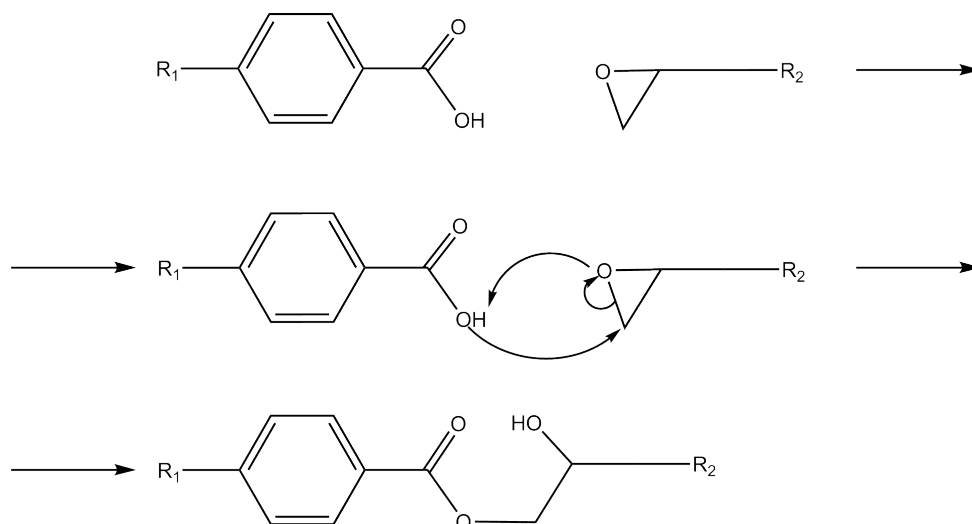


Figure 2.7: Epoxide and carboxylic acid reaction mechanism

Japon et. al. studied chain extension of PET using tri-, tetre- and multifunctional

epoxide compounds and reported significant increase of intrinsic viscosity for the tri- and tetrafunctional compounds [27].

2.4.3 Maleic anhydride chain extenders

Chain extenders with maleic anhydride as the reactive functionality have been the subject to extensive research [35, 36, 37]. Maleic anhydride compounds show selective reactivity towards the hydroxyl end group of PET according to the anhydride ring opening mechanism presented in Figure 2.8, which is initiated by a nucleophilic attack of a hydroxyl end group of PET on either of the anhydride carbon atoms. The reaction yields one chain extended segment via esterification and a new carboxyl end group. This carboxylic acid may react with another hydroxyl end group via the Fischer esterification mechanism but the reaction rate for this step is much lower [36]. Due to this difference in reaction rate, the practical functionality of the anhydride of maleic anhydride is closer to one than two. Furthermore the second esterification reaction results in the formation of a water molecule which may add to the degradation of PET via hydrolysis.

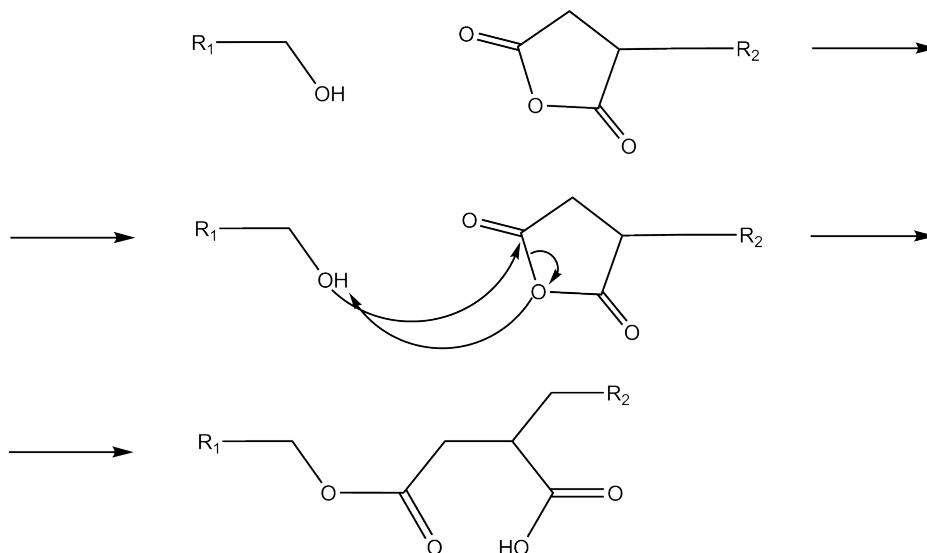


Figure 2.8: Maleic anhydride and hydroxyl reaction mechanism

There are several varieties of maleic anhydride chain extenders, including di, tri, tetra and multi-functional species. The simplest form is pure maleic anhydride which renders reactive sites both at the anhydride segment and at the double bond [35]. Pyromellitic dianhydride, PMDA, a tetra-functional chain extender has been studied intensively and shows significant increase in intrinsic viscosity at concentrations of 0,3 wt% but the effect reverses if more than 1 wt% is added [36, 37]. Multifunctional maleic anhydride chain extenders for PET have thus far been left uninvestigated in academia, but there are commercial varieties aimed at upgrading polyamide that theoretically could work for PET as well.

2.4.4 Oxazoline chain extenders

Compounds with oxazoline functional groups provide chain extending ability selectively with the carboxyl end groups of PET. The chain extending reaction follows the oxazoline ring opening mechanism where the carboxyl end group of PET performs a nucleophilic attack on the electrophilic carbon atom next to the oxygen atom shown in Figure 2.9 [28]. Side reaction products have been recorded but they too are of branching character. Acid compounds are the main factor in the by product formation of oxazolines.

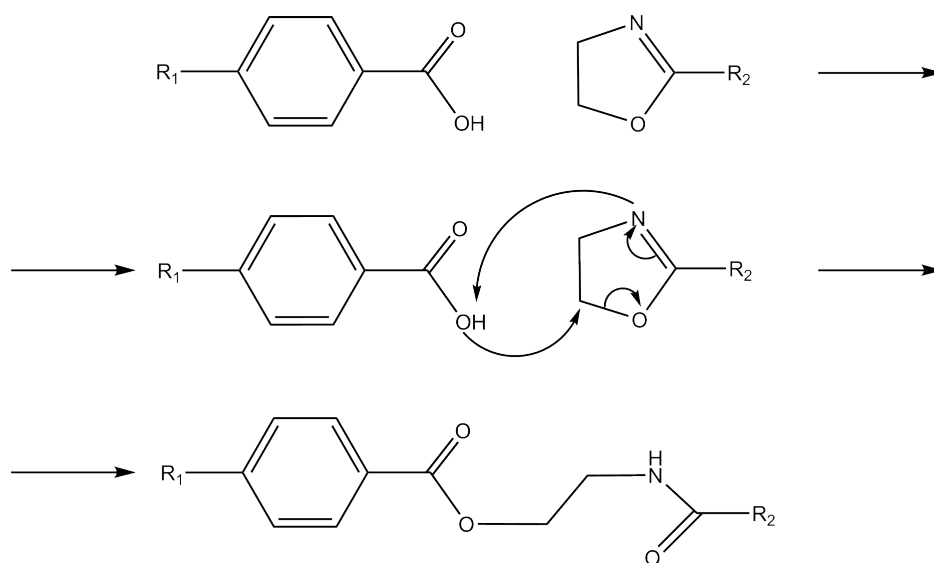


Figure 2.9: Oxazoline and carboxylic acid reaction mechanism

Inata et. al. investigated PET chain extension with a variety of oxazoline compounds and concluded that bis-2-oxazolines were among the most efficient compounds based on sharp increases in intrinsic viscosity [28]. Furthermore, Veselova et. al. investigated PET chain extension with 1,3-phenylene-bis-oxazoline, PBO, and reported a significant increase in molecular weight and a decrease in melt flow index at 0,1 wt % addition of PBO.

2.4.5 Oligomeric chain extenders

Oligomeric chain extenders offers both high chain extending functionality as well as polymer segments with properties that enhance the processability. With increasing chain extending functionality the risk of onset of gelation increases with poor mechanical properties as a result [30]. Therefore, the level of functionality is a limiting factor. However, for an oligomeric chain extender with a high degree of polydispersity, a high degree of branching can be achieved without immediate initiation of gelation. The high degree of polydispersity, with an optimum mixture of low and high functional chains, enables moderate branching reactions [38].

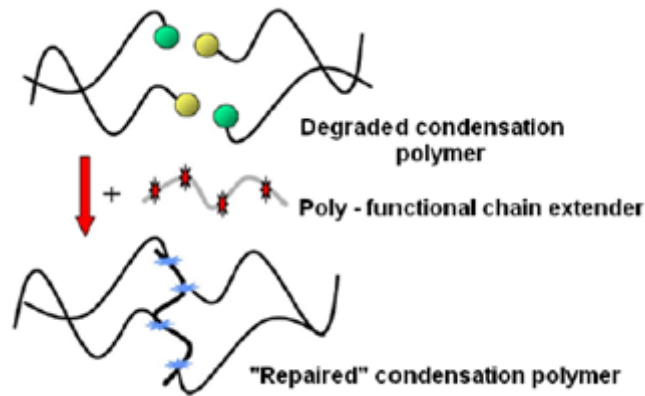


Figure 2.10: Principle reaction scheme for an oligomeric chain extender [9].

2.5 Glass fiber

Glass fibers are commonly used as reinforcement in polymers to create high strength materials referred to as fiberglass. The orientation of the glass fibers in the composite material is an important factor determining the directional mechanical properties and are improved along the fiber axis compared to across the axis. The properties for a composite material with random orientation of fibers will have little orientation dependence, but the orientation distribution varies in the material and gives rise to local weak points in the material. Ferenc Ronkey investigated PP/PET blends of varying compositions and the addition of 9 wt% glass fibers and report an increase in tensile strength of 138 % for a 70/30 wt% ratio of PP/PET [39].

As a finishing step in the production of glass fibers, a sizing is applied to regulate the surface properties suitably for the intended application. For fiberglass composites the glass fibers are applied with coupling agents that increase the compatibility between the glass fibers and the polymer matrix. Compatibility is achieved by complete wetting of polymer on the glass fibers and good adhesion between the two. There are a variety of adhesion increasing sizings available of whom most are based on compounds with a silane segment and a coupling segment that can be epoxy, methacrylate, vinyl, diamine or other functional groups that can be tailored for specific composite applications [40].

2.6 Reactive extrusion

Reactive extrusion is performed by using the extruder as a reactor. During reactive extrusion the polymers are melted, mixed and reaction of PET end groups with chain extending compounds can take place. The process is schematically illustrated in Figure 3.6. Due to the versatility of the process, reactive extrusion is widely used for recycling of polymers and polymer blends [25]. The process is complex because of the many parameters that can be varied and the most important are screw configuration, screw speed, residence time and temperature. The polymer degradation in reactive extrusion is mainly dependent on residence time and temperature. The temperature

should be chosen so that the polymers are completely melted but higher temperature will contribute to degradation. However, the reaction yield between chain extender and PET end groups is also dependent on residence time. Thus the residence time has to be optimized in order to maximize the chain extension reaction and minimize the degradation [9]. For reactive extrusion of PET, the hydrolytic degradation can be reduced by equipping the extruder with a vacuum degassing system, which removes volatile substances such as water. The screw speed and screw configuration determine the degree of mixing, which is an important factor for the degree of dispersion and for the chain extenders to encounter the PET end groups.

2.7 Summary

Based on the literary review it was found that epoxy, maleic anhydride and oxazoline chain extenders were among the most efficient and di- and multifunctional PET chain extenders are therefore of interest. However, the compounds used in the study should meet certain requirements. The chain extenders used need to be non toxic, solid, thermally stable and commercially available to a reasonable cost, because the model system is investigating recycling of PP/PET blends for industrial scale production. This leaves limited candidates to be studied. Polymeric type chain extenders with epoxy and maleic anhydride functionalities and a solid difunctional oxazoline compound, 1,3-phenylene-bis-oxazoline, were chosen since they were composed of interesting chemical groups for the study and met the criteria above. PP/PET wt% ratio of 70/30 was chosen to achieve a continuous PP matrix and to have high enough PET content in order for it to influence the material properties. No previous studies of chain extension of a dispersed PET phase in a compatibilized a PP/PET system have been found.

3

Experimental

3.1 Materials

The materials used in this master's thesis project are presented in Table 3.1 and include four types of components; PET, PP, compatibilizing agents and chain extenders. The chemical structures of the materials and their respective monomer content are presented in figures 2.1, 2.4 and 3.2 - 3.5.

Table 3.1: Trade name, chemical description and supplier for the materials used.

Trade name	Chemical description	Supplier
Wellman 1330	PET fibers	Wellman International
HH450FB	PP pellets	Borealis AG
Lotader AX 8900	ethylene- acrylic ester- glycidyl methacrylate random terpolymer	Arkema SA
Epolene G 3015	Maleic anhydride grafted polypropylene	Eastman
Joncryl ADR4469 HP	styrene- acrylic ester- glycidyl methacrylate random terpolymer	BASF SE
Nexamite PBO	1,3-phenylene-bis-oxazoline	Nexam Chemical AB
Zemac Extend M600	ethylene- maleic anhydride alternating copolymer	Vertellus Specialties
ER10VC	E-Glass fibers	Chongqing Polycomp I.C

The model system study of the recyclability of compression molded PP and PET features was performed with a homopolymeric PP of fiber-quality and the PET was a standard type of PET fiber. The choice of compatibilizing agents was based on a literary review and resulted in a glycidyl methacrylate type, Lotader AX 8900, and a maleic anhydride variety, Epolene G 3015. Unfortunately a glycidyl methacrylate functionalized compatibilizer with PP segments was not found commercially and therefore an ethylene substitute, Lotader AX 8900 was chosen. The chain ex-

tenders investigated were also chosen based on the literary review which concluded that epoxy, maleic anhydride and oxazoline compounds were of interest, as well as investigating di- and multifunctional compounds.

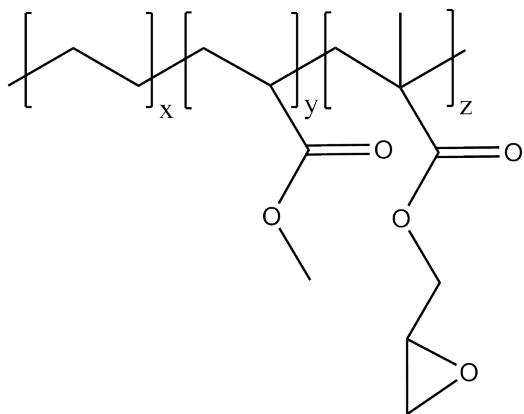


Figure 3.1: Chemical structure of Lotader AX 8900.

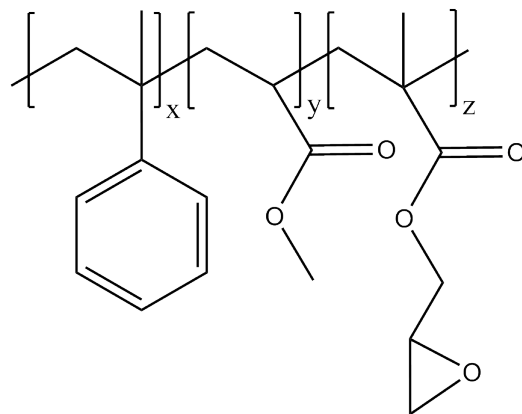


Figure 3.2: Chemical structure of Joncryl ADR4469 HP

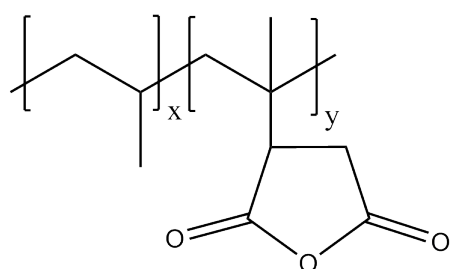


Figure 3.3: Chemical structure of Epolene G 3015

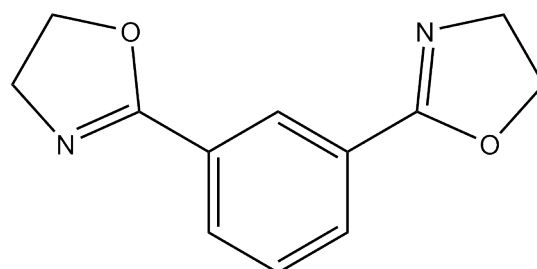


Figure 3.4: Chemical structure of Nexamite PBO

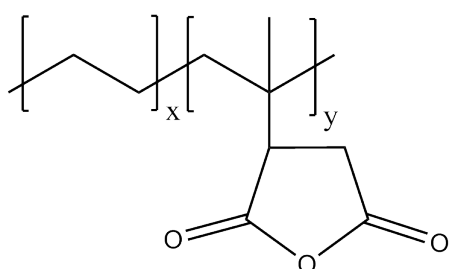


Figure 3.5: Chemical structure of Zemac Extend M600

3.2 Sample processing

The production of PET and PP blend samples with compatibilizing agents and chain extenders include several steps. First, processing of the PET fibers, followed by twin-screw reactive extrusion where the components are blended, reacted and then granulated. The granules produced were finally injection molded into standardised tensile specimens.

3.2.1 PET fiber preparation

The fluffy fiber mass was processed into sturdy strands in order to enable controlled feeding of the PET fibers into the extruder. This was done by initially carding the PET fibers in a laboratory carding machine Cormatex CC/400 and then needle punched on a laboratory needle punch machine Certec model 38 followed by cutting into strands suitable for extrusion feeding on a guillotine paper cutter.

3.2.2 Twin-screw reactive extrusion

PET fibers, PP pellets, compatibilizing agent pellets and chain extenders in pellet or powder form, were reactively extruded in a Werner Pfleiderer ZSK26 (Coperion Corporation) co-rotating twin-screw extruder with a screw diameter of 25 mm and a L/D ratio of 40. The setup of the process is illustrated in Figure 3.6. The screw configuration was composed of three mixing elements and two reversed conveying elements. The screw speed was 200 rpm and a vacuum degassing system continuously removed volatile compounds. The temperature profile of the ten screw segments was 165-260-260-260-260-260-260-250-240-240 °C. PP pellets and compatibilizing agents were inserted into the extruder with a K-Tron gravimetric feeder. The PET fibers strands were introduced manually. The PET fibers were dried before they were added in the extruder in a XD3 dehumidifying dryer (Moretto) for 90 minutes at 140 °C with dry air flow of 60 cm^3/s . Chain extenders were added by a in-house designed single screw feeder calibrated for each substance.

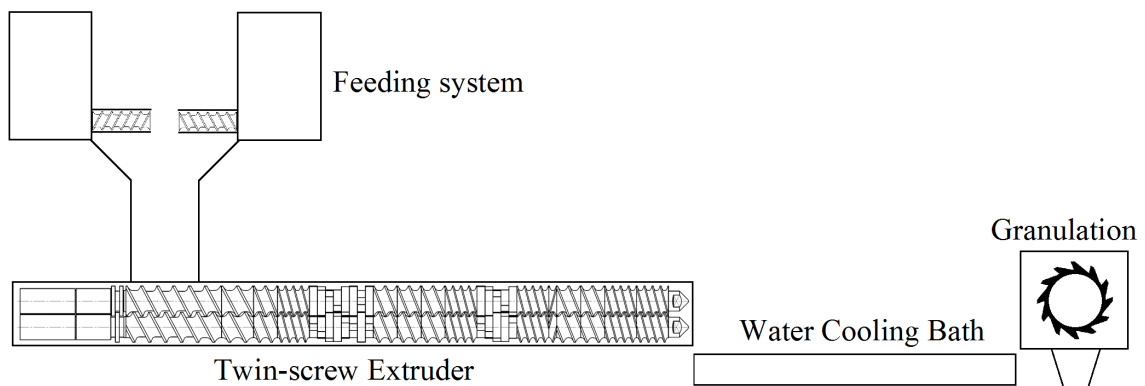


Figure 3.6: Reactive extrusion process setup.

The blends produced were composed of a PP/PET ratio of roughly 70/30 in order to maintain PP as the continuous phase. Compatibilizing agent, chain extender and glass fiber were added according to table 3.2. After reactive extrusion the polymer blends were granuled in a lab size pelletizer model SGS 25-E4 (SF Scheer).

Table 3.2: Blend compositions produced in reactive extrusion. The unit for all columns is (wt%).

Sample	PP	PET	Compatibilizers		Chain extenders			GF
			Lotader	Epolene	Joncryl	PBO	Zemac	
0	66,9	33,1						
1,5E	65,1	33,4		1,5				
3E	64,5	32,5		3,0				
3L	65,2	31,8	3,0					
5L	63,2	31,8	5,0					
0,7J	68,2	31,1			0,7			
0,4P	68,5	31,1				0,4		
5Z	63,4	31,4					5,0	
3L 0,3J	66,6	30,1	3,0		0,3			
3L 0,5J	65,1	31,4	3,0		0,5			
3L 0,7J	64,9	31,5	3,0		0,7			
3L 5Z	64,7	32,2	3,0				5	
5L 0,7J	63,2	31,1	5,0		0,7			
5L 0,2P	63,7	31,1	5,0			0,2		
5L 0,4P	63,6	31,1	5,0			0,4		
1,5E 0,7J	66,3	32,2		1,5	0,7			
1,5E 0,2P	65,8	32,7		1,5		0,2		
1,5E 0,4P	67,1	31,4		1,5		0,4		
3E 0,7J	63,8	32,5		3,0	0,7			
3E 0,2P	63,8	33,2		3,0		0,2		
3E 0,4P	64,6	32,3		3,0		0,4		
3E 10GF 0	87,4			3,0				9,6
3E 15GF 0	81,9			3,0				15,1
3E 10GF	61,8	28,2		3,0				10,1
3E 10GF	61,6	28,4		3,0		0,4		10,2
0,7J 0PP		99,3			0,7			

3.2.3 Injection molding

Specimens for mechanical testing were produced in an injection molding machine model ES 200/110 HL-V (Engel). The blend granules were dried for 16 hours at 120 °C in dehumidified air before injection molding. The temperature of the screw was 260 °C and the mold temperature was 20 °C. The injection rate was 25 cm³/s, holding pressure time was 25 s and the cooling time was 10 s. The pressure needed to fill the mold varied for different samples ranging from 160 to 290 bar.

3.2.4 Glass fiber content determination

The glass fiber content of the samples containing glass fibers was determined by calcination. The samples were heated over night at 550 °C and the sample was weighed before and after calcination.

3.3 Characterization

The stress at yield, young's modulus and strain at yield were determined on a MTS universal testing machine model 20/M in accordance with ISO standard 527. Impact strength was determined by a Ceast 9050 impact pendulum (Instron) according to the ISO 179 standard.

Glass transition temperature, crystallization and melting behavior were analyzed by differential scanning calorimetry, DSC, on a Star system DSC 1 machine (Mettler Toledo). The temperature program was first set to heating from 25 °C to 300 °C at 10 °C/min to get the same thermal history for all samples. They were then cooled to 25 °C at 5 °C/min to register the crystallization enthalpies, followed by heating again to 300 °C at 5 °C/min, during which the melting enthalpies were recorded. The degree of crystallinity was determined from the DSC analysis by equation 3.1

$$Crystallinity = \frac{\Delta H_m}{\Delta H_m^{\circ}} \cdot 100 \quad (3.1)$$

where ΔH_m is the energy of melting extracted from the DSC analysis and ΔH_m° is the theoretical energy of melting for a 100 % crystalline polymer. The ΔH_m° value for PP and PET are 207,1 J/g respectively 140,1 J/g [41].

FTIR (Tensor 27, Bruker) was used to study the chemical bonds in the blends produced, and whether the chain extension reaction was reacting as proposed. The spectra of absorption peaks from molecular bond vibrations could indicate the degree of reaction that had taken place. The resulting spectra were baseline corrected and mathematically fitted to a standard peak at 1454 cm^{-1} corresponding to the C-C bonds of PP.

Finally the microstructure of the surface of impact fractured and argon ion milled specimens were analysed by scanning electron microscopy, SEM, on a JSM-6610LV scanning electron microscope (Jeol). Images were taken with secondary electron- and backscattered electron detection modes.

4

Results

The results in this master's thesis work comprise of data collected from infrared analysis, differential scanning calorimetry, scanning electron microscopy and mechanical analysis.

4.1 Fourier transform infrared spectroscopy

The PET chain extension reactions of Joncryl, PBO and Zamac where analysed by FTIR and the resulting spectra support the theory of the chain extenders selective reactivity towards respective PET end groups.

In Figure 4.1 the blend with 5 % Zamac shows an increase compared to the reference blend in the broad absorption peak at 1240 cm^{-1} corresponding to the C-O bond of carboxylic acid and a decrease in the 1020 cm^{-1} and 1100 cm^{-1} absorption peaks corresponding to the C-O bond of hydroxyl [42]. These shifts in absorption agree with the mechanism proposed in Figure 2.8 for the reaction of maleic anhydride with the hydroxyl end group of PET.

The spectrum for the blend with 0,4 % PBO in Figure 4.1 shows an increase compared to the reference blend in the absorption peak at 1580 cm^{-1} that corresponds to the N-H bond of amine and a slight decrease in the absorption peak at 1240 cm^{-1} corresponding to the C-O bond of carboxylic acid [42]. These shifts in absorption agree with the mechanism proposed in Figure 2.9 for the reaction of oxazoline with the carboxylic acid end group of PET.

The blend with 0,7 % Joncryl, with the infrared spectrum depicted in Figure 4.1, shows an increase in the absorption peaks for hydroxyl C-O bonds at 1020 cm^{-1} and 1100 cm^{-1} and a slight decrease in the absorption peak for the carboxyl acid C-O bond at 1240 cm^{-1} . These shifts in absorption agree with the mechanism proposed in Figure 2.7 for the reaction of epoxide with the carboxylic acid end group of PET.

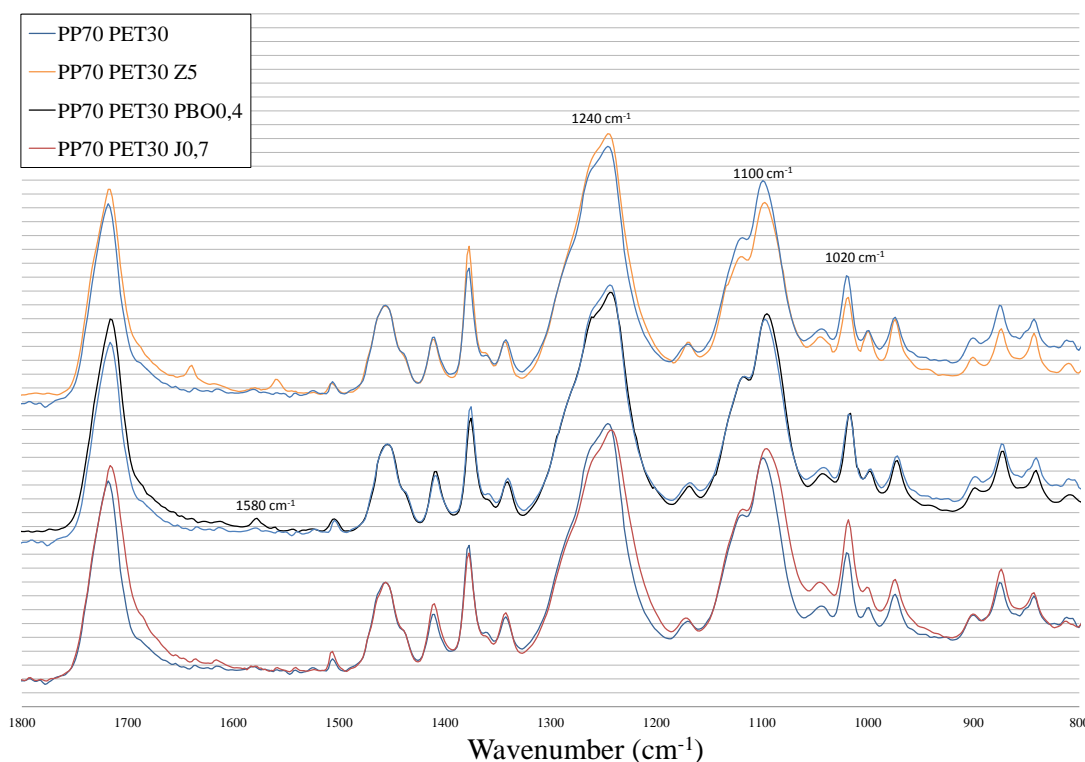


Figure 4.1: Infrared spectra of blends with 5 wt% Zemac, 0,4 wt% PBO and 0,7 wt% Joncryl along with a reference blend.

4.2 Differential scanning calorimetry

The crystallinity of PP and PET was determined for granules of reactively extruded blends before injection molding. The crystallinity of the PP phase is presented in Figure 4.2. The uncompatibilized PP/PET blend had a PP crystallinity on the same level as pure PP. Addition of Lotader increased the crystallinity slightly with increasing concentration. The chain extender Joncryl combined with Lotader increases the PP crystallinity further. Addition of compatibilizer Epolene to PP/PET increases the crystallinity of PP, especially at 3 wt% Epolene. Combining Epolene with addition of chain extenders Joncryl or PBO further increases the crystallinity of the PP phase. The highest crystallinity was reached with addition of 3 wt% Epolene and 0,2 wt% PBO.

The crystallinity of the PET phase for the blends produced, presented in the appendix in Figure A.4, are clearly affected by addition of both compatibilizer agent and chain extender but there does not seem to be any apparent trends.

DSC thermograms of the polymer blends produced shows a large difference in the nucleation of of PP and PET crystals for the different polymer blends. Addition of compatibilizer and of chain extender clearly has an effect on the nucleation behavior. However, interpretation of the results requires more analyses and is out of the scop

of this project. The Figures are presented in the appendix A.1 - A.3.

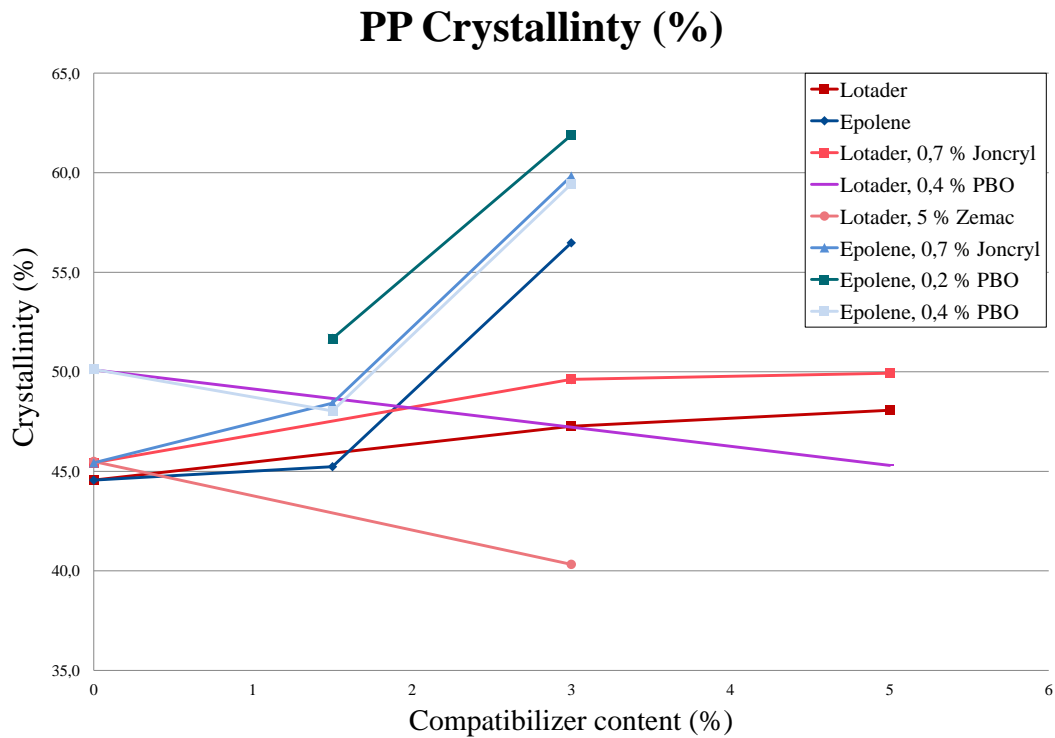
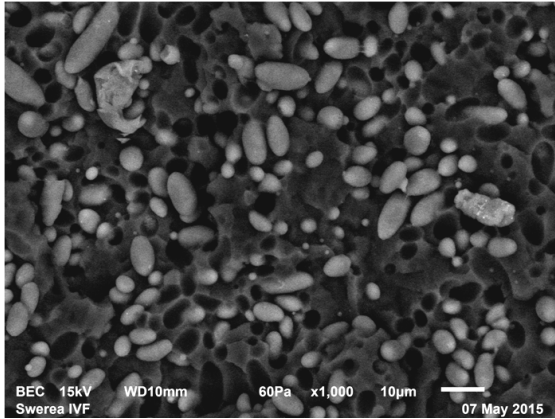


Figure 4.2: PP degree of crystallinity.

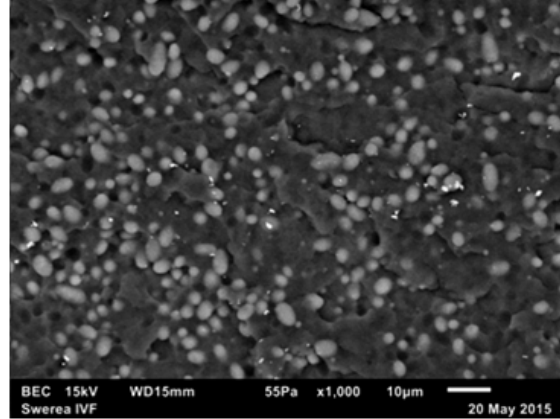
4.3 Scanning electron microscopy

The fracture surfaces of test bars that were subject to impact strength test were studied by SEM. Visual The micrograph of the uncompatibilized blend with 70/30 wt% PP/PET, Figure 4.3a, shows a dispersed PET phase with distorted ellipsoid shapes with particle sizes of about $10 \mu m$. Also, the cavities in the PP matrix from PET particles ablated from impact measurement are well defined. The SEM image of the blend with 1,5 wt% Epolene added, Figure 4.3b, shows a higher dispersion of the PET phase with a more even particle size distribution with particle sizes of $3 \mu m$. The remnant cavities in the PP from impact fracturing are less defined than for the uncompatibilized blend. The micrograph of the blend with 3 wt% Epolene, Figure 4.3c shows even higher dispersion with dispersed PET drops of $2 \mu m$ in size, and low definition of cavities in the PP matrix.

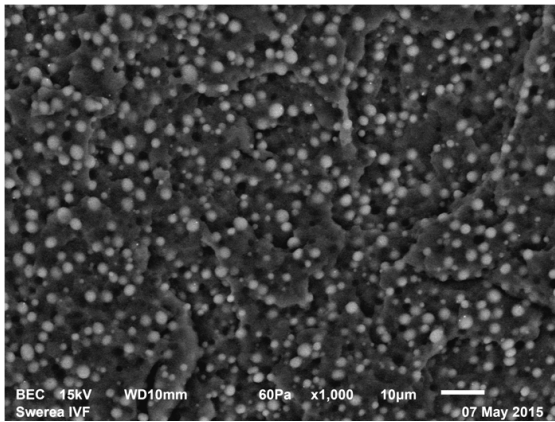
The SEM image of the blend with 3 wt% Lotader, Figure 4.3d, show finely dispersed PET spheres which seem to have agglomerated into particles of about $10 \mu m$ in size. The cavities in the PP phase are less prominent than in the blend without additives but more than the blend with 3 wt% Epolene.



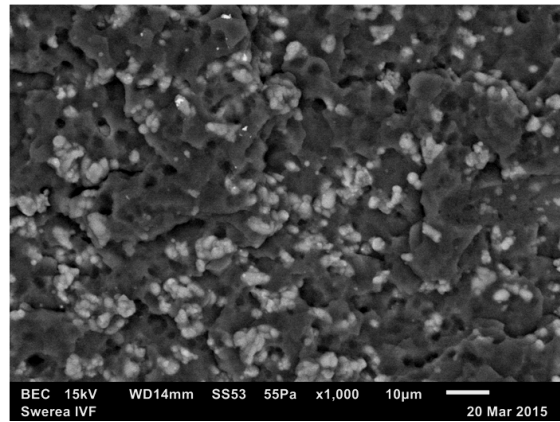
(a) PP/PET 70/30.



(b) PP/PET 70/30 with 1,5 wt% Epolene.



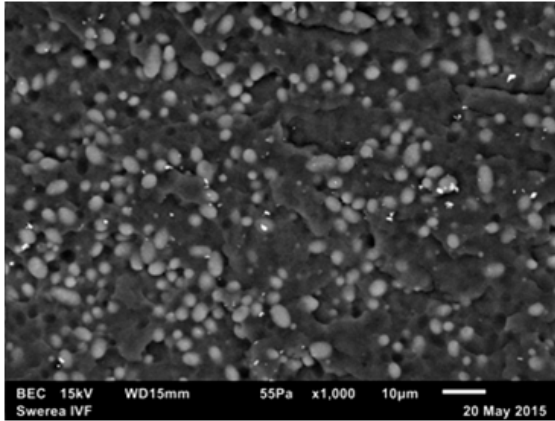
(c) PP/PET 70/30 with 3 wt% Epolene.



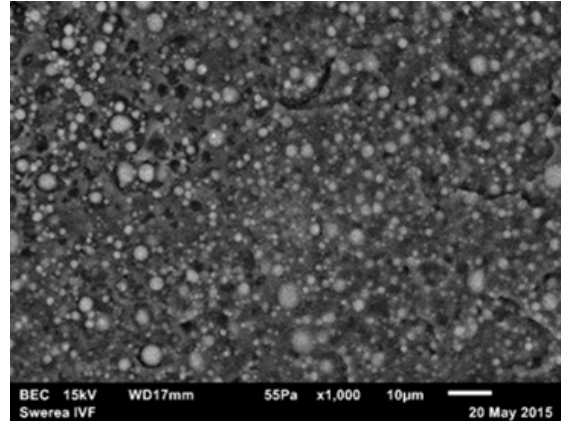
(d) PP/PET 70/30 with 3 wt% Lotader.

Figure 4.3: Scanning electron micrographs of impact fractured surfaces of an uncompatibilized blend and compatibilized blends. In the images above PP is dark grey and PET is light grey and the white bar corresponds to 10 μm

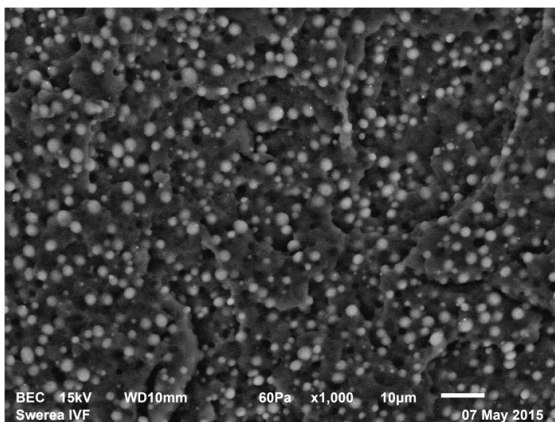
The micrograph of a blend with Epolene combined with Joncryl, Figure 4.4b, compared to a blend with only Epolene, Figure 4.4a, shows a significant increased dispersion of the PET phase with PET spheres measuring 1 μm in size, but with a somewhat larger particle size distribution. The degree of cavities in the PP matrix are similar in the two micrographs. For a blend with combination of Epolene and PBO, Figure 4.4d, compared with a blend with only Epolene added, Figure 4.4c, the dispersion has remained unaffected. The degree of cavities of the two blends are similar as well.



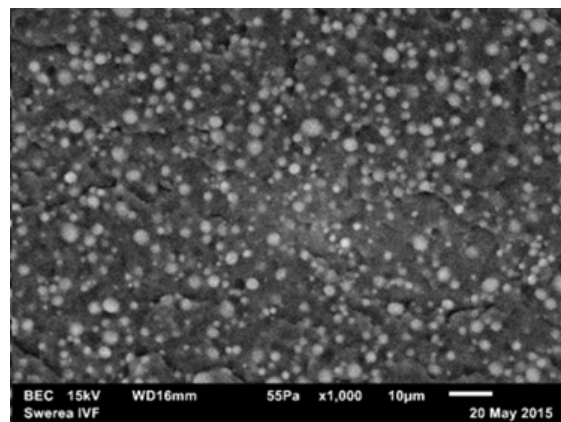
(a) PP/PET 70/30 with 1,5 wt% Epolene.



(b) PP/PET 70/30 with 1,5 wt% Epolene and 0,7 wt% Joncryl.



(c) PP/PET 70/30 with 3,0 wt% Epolene.



(d) PP/PET 70/30 with 3 wt% Epolene and 0,4 wt% PBO

Figure 4.4: Scanning electron micrographs of impact fractured surfaces of compatibilized blends and combination of compatibilized and chain extended blends. In the images above PP is dark grey and PET is light grey and the white bar corresponds to $10\ \mu\text{m}$

4.3.1 SEM micrographs of effects from injection molding

A specimen with PP/PET ratio of 70/30 and 3 wt % Lotader compatibilizer was argon ion milled to obtain a polished cross section. The micrograph of a cross section of the specimen, presented in Figure 4.5, reveals a spherical dispersed and somewhat agglomerated PET phase in a PP matrix. The micrograph of a cut section along the specimen, Figure 4.6, shows slightly elongated ellipsoid geometry, which is remnant from the flow history during the injection molding process.

The micrograph of a PP/PET blend compatibilized with 1,5 wt% Epolene, Figure 4.7, shows the edge of the impact fractured cross section. The dispersed light grey PET spheres in the dark grey PP matrix are elongated parallel to the surface, and the elongation increases closer to the surface of the test bar. The elongation of the PET phase extends $60\ \mu\text{m}$ from the surface of the test bar.

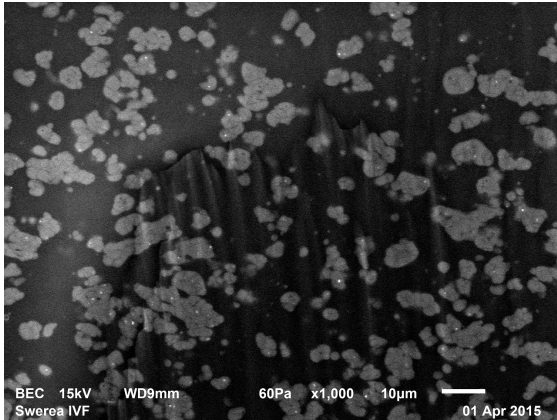


Figure 4.5: Scanning electron micrograph of the across the specimen.

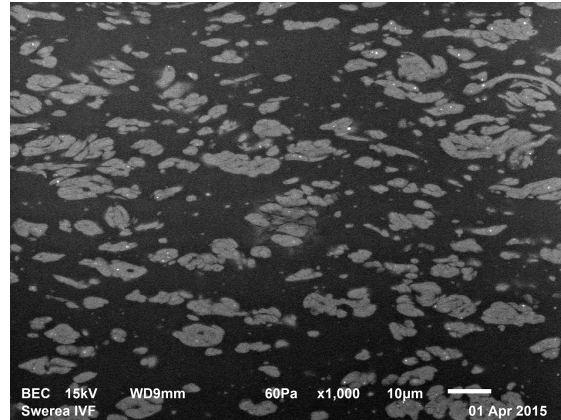


Figure 4.6: Scanning electron micrograph of the along the specimen.

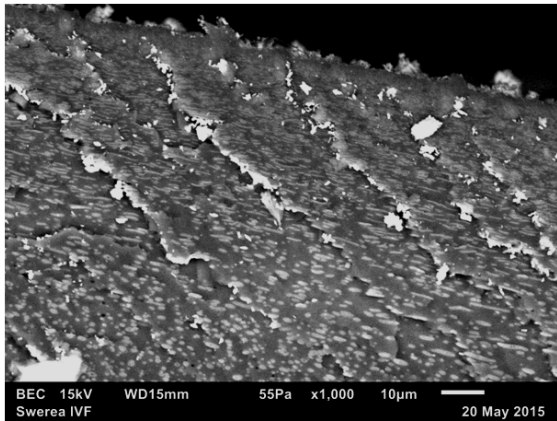


Figure 4.7: Scanning electron micrograph of the edge of a PP/PET 70/30 blend with 1,5 wt% Epolene.

4.4 Mechanical analysis

Young's modulus, strain at yield, stress and break at yield and impact strength were investigated on standard specimens for all of the blends produced. Reference measurements were made on PP and glass fiber reinforced PP.

4.4.1 Young's modulus

The Young's modulus vs compatibilizer content for of blends with PP/PET and chain extender are presented in Figure 4.8. Pure PP had a modulus of 1414 MPa and an uncompatibilized blend had a Young's modulus of 1784 MPa. The Young's modulus decreased significantly for blends with compatibilizer Lotader and increased with compatibilizer Epolene. Combining respective compatibilizing agent with chain extenders slightly effects the modulus.

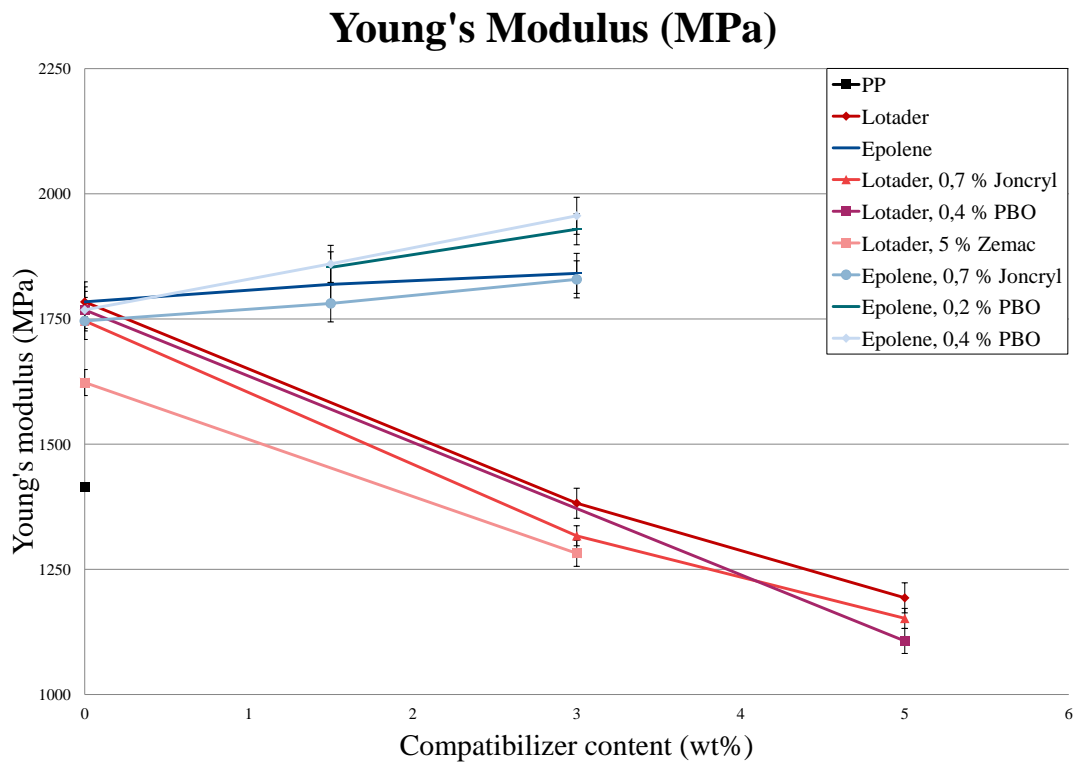


Figure 4.8: Young's modulus of blends with varying component compositions.

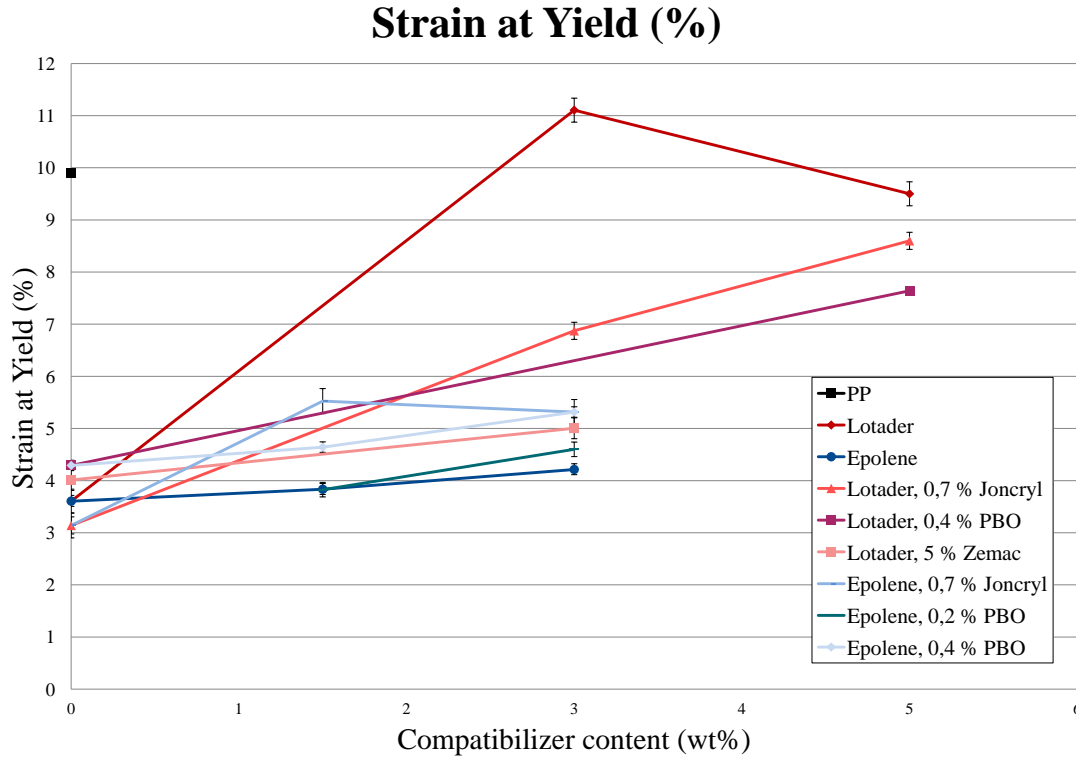


Figure 4.9: Strain at yield of blends with varying component compositions.

4.4.2 Strain at yield

The strain at yield for PP/PET blends and chain extender are presented in Figure 4.9. The yield strain for the uncompatibilized blend was significantly lower than for pure PP. Blends with Lotader significantly increases the strain at yield especially at 3 wt%. Combining chain extenders with Lotader reduces the yield strain compared to the blend with Lotader significantly. Blends compatibilized with Epolene increased slightly in strain at yield and blends with Epolene combined with chain extenders registered an increased strain at yield compared to the blend with only Epolene.

4.4.3 Stress at yield and stress at break

The stress at yield is presented for the blends produced since it defines when the material has lost its integrity. The stress at break is shown for the blends produced with glass fiber reinforcement since they did not reach a yield point during deformation. The stress at yields of blends with PP/PET and chain extender are presented in Figure 4.10 with varying compatibilizing agent concentrations. The stress at yield for an uncompatibilized blend is lower than that of pure PP.

With 3 wt% addition of the compatibilizer Lotader the stress at yield was unaffected compared to the uncompatibilized blend, but with 5 wt % it was decreased. Combining compatibilizer Lotader with chain extenders; Joncryl, Zamac and PBO, reduces the stress at yield compared to the blend where only Lotader was added.

Epolene compatibilized blends result in significantly increased stress at yield, especially at 3 wt%. By combining Joncryl with Epolene a large increase in the stress at yield was obtained. PBO in combination with Epolene also increased the stress at yield significantly.

Figure 4.11 shows the stress at break for the glass fiber reinforced blends. Two reference blends of PP with 10 and 15 wt% glass fiber were prepared. A blend with PP/PET wt% ratio of 70/30 and 10 wt% glass fiber obtained higher stress at break than the reference PP blend with 10 wt% glass fiber. Addition of PBO increased the stress at break further.

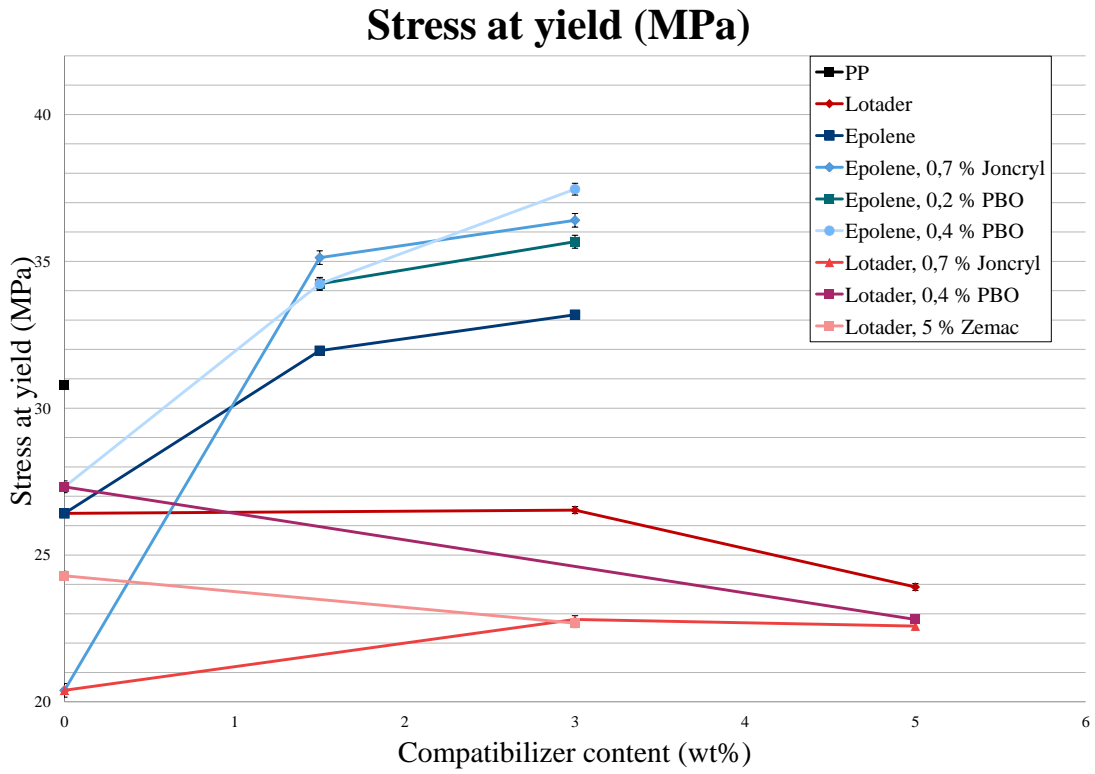


Figure 4.10: Stress at yield of blends with varying component compositions.

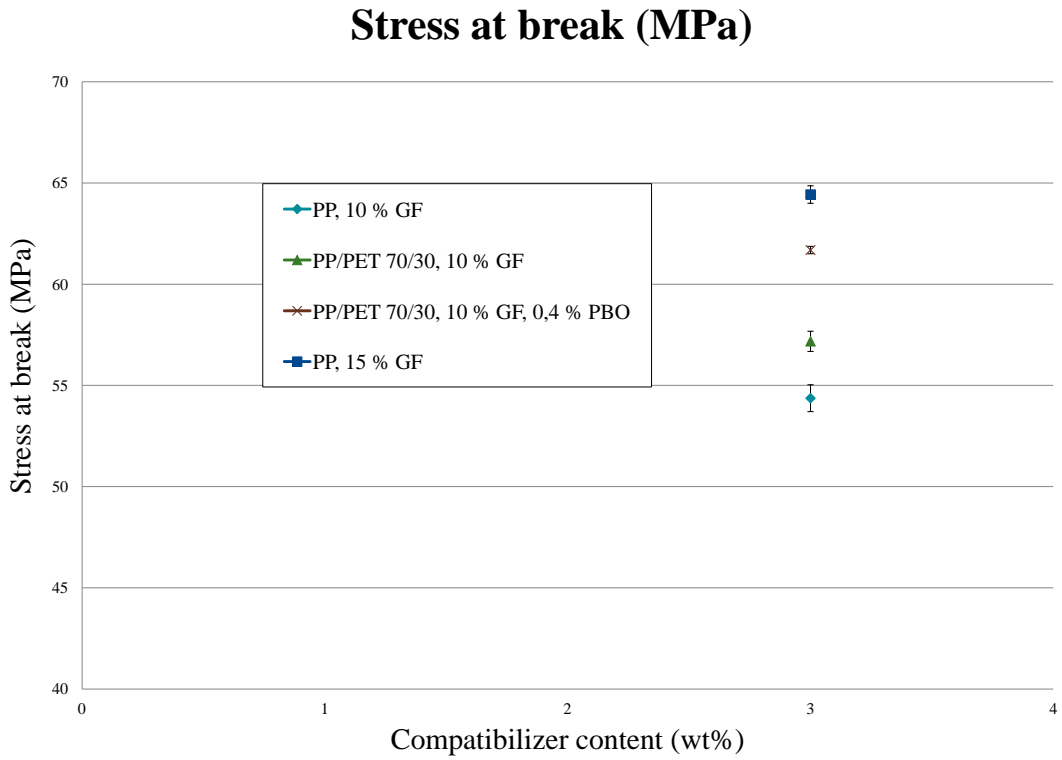


Figure 4.11: Stress at yield of glass fiber blends with with varying component compositions.

4.4.4 Impact strength

The impact strengths of un-notched PP/PET blends are presented in Figure A.5 in the appendix and shows increasing impact strengths with practically any additive. Notched impact strength tests, presented in Table 4.1 showed that the impact strength for the uncompatibilized PP/PET blend was significantly lower than that of pure PP. A blend with 3 wt% Epolene and 0,4 wt% PBO retrieved the impact strength close to pure PP.

Table 4.1: Impact strength of notched PP and PP/PET blends with wt% ratio of 70/30.

Sample	Impact strength (MPa)
PP	1,81
PP/PET	1,20
PP/PET 3 wt% Epolene 0,4 wt% PBO	1,72

5

Discussion

5.1 Indication of chain extension

The degree of reaction of reactively extruded blends evaluated with FTIR indicate that the chain extenders react according to the mechanisms proposed in Figure 2.7, 2.8 and 2.9. This indicates that the degree of mixing and the residence time in the reactive extrusion process were sufficient for the chain extenders to be able to diffuse through the PP matrix and react with PET end groups to a high extent. The intense mixing is achieved by high shear due to mixing elements in the extruder and high screw speed. High shear is a prerequisite for creating high dispersion in the polymer blend.

5.2 The effect of microstructure and crystallinity on the mechanical properties

The increase in dispersion for blends compatibilized with Epolene, Figure 4.3a - 4.3c, shows that Epolene is highly surface active. Also, the absence of clearly defined cavities for blends with compatibilizer Epolene indicates an increase in adhesion of the PP and PET phase, resulting from that PP segments from Epolene entangle in the PP phase.

Increased dispersion, which means a decrease in the size of the dispersed phase droplets, results in a higher interfacial area between PP and PET. The maleic anhydride groups of Epolene react with the PET phase forming strong covalent bonds. The PP segments of Epolene can interact with the PP in the matrix and is retained there by intergration in crystallites, steric entanglement and by intramolecular forces. The degree to which the PP segments of Epolene is retained in the PP matrix combined with the maleic anhydride group of Epolene forming covalent bonds with the PET phase contributes to increasing the strength of the material, and enables the PET phase, which has higher strength than PP, to contribute to increasing the overall strength.

The significant increased dispersion for the blend with both compatibilizer Epolene and chain extender Joncryl indicate that Joncryl is a surface active substance and that the surface activity for Epolene and Joncryl is synergetic. The surface activity

for Joncryl could be due to the olefinic backbone of the copolymer interacting with the PP phase whilst the polar styrene, vinyl acetate and glycidyl methacrylate segments interact with the PET phase.

The changes in dispersion, both for blends with Epolene and Epolene combined with Joncryl, show positive correlation with the stress at yield, where increased dispersion leads to higher stress at yield. Combination of compatibilizer Epolene with chain extender PBO seemed not to change the degree of dispersion, indicating that PBO is not surface active but rather prefers the PET phase.

The crystallinity of the PP phase shows a positive correlation with increase in compatibilizer content, shown in Figure 4.2. The effect is greatest for the compatibilizer Epolene, especially at 3 wt%. Since PP constitutes the matrix, the crystallinity of PP influences the material strength. The increase in crystallinity can be explained by the Epolene PP segments entanglement in the PP phase where it possibly could initiate crystallization. Compatibilizer Lotader entangles less in the PP phase and would therefore initiate less crystallization. For the blends with the highest stress at yield with combination of 3 wt% Epolene and PBO the significant increase in stress at yield can be connected to the drastic increase in PP crystallinity. The synergetic effect on PP crystallinity for blends with Epolene and chain extender is not fully understood and need further investigation.

The blend with compatibilizer Lotader, where the dispersed PET phase seems to have aggregated to 10 μm particles, Figure 4.3d, indicate poor compatibility between the phases. The Young's modulus was increased for blends with Epolene and decreased for blends with Lotader, indicating that Epolene compatibilizes the PP phase with the PET phase more efficiently than Lotader. The lack of adhesion bet PP and PET phases for the blends with Lotader is illustrated by the dramatic increase in strain at yield.

The stress at yield increased by 26 % for the blend with 3 wt% Epolene compared to uncompatibilized blend. Addition of 3 wt% Epolene and 0,4 wt% PBO resulted in an increase of 42 % compared to the uncompatibilized blend. Razak et. al. investigated PP/PET compatibilization with a MA-compatibilizer and obtained a 13,5 % increase in tensile strength. The significantly lower increase in tensile strength could be a result of a too high extrusion temperature, 285 °C, leading to degradation, and a much slower screw speed, 50 rpm as compared to 200 rpm in this study, resulting in worse dispersion [19].

Ronkay et. al. observed that a PP/PET blend with 70/30 wt% ratio with 9 wt% glass fiber increased the tensile strength 20 % compared to PP with 9 wt% glass fiber. In this diploma work, the PP/PET blend of 70/30 wt% ratio with 3 wt% Epolene and 10 % glass fiber showed a 5 % higher stress at break than a blend with PP, 3 wt% Epolene and 10 % glass fiber.

5.2.1 The effect of injection molding on the microstructure

The micrographs of a test bar along and across the cross section, Figure 4.5 & 4.6 show noticeable anisotropy in the PET phase dispersion. However, the degree of anisotropy is probably not high enough to significantly affect the material properties. A micrograph of the cross section of an injection molded test bar, Figure 4.7 shows elongated PET domains close to the surface which gradually changes to spherical shape in the bulk. The anisotropy and the elongation of the dispersed phase close to the surface are remnant effects from the polymer melt flow during injection molding. The microstructure at the surface will be affected by the injection molding process and will probably have an influence on the un-notched impact strength.

6

Conclusions

PP and PET blends with higher stress at yield than pure PP have been developed through compatibilization and chain extension. The polymer blends can be produced by feeding the components in an industrial size extruder.

Two compatibilizing agents were evaluated, of which Epolene, a maleic anhydride grafted polypropene, was determined to be most effective. Three chain extenders were evaluated, of which PBO, 1,3-phenylene-bis-oxazoline, and Joncryl, a styrene-vinyl acetate-glycidyl methacrylate copolymer, were the most efficient. The highest stress at yield was observed for the blend with 3 wt% Epolene and 0,4 wt% PBO, increasing stress at yield 42 % compared to an uncompatibilized blend. Even less additives, 1,5 wt% Epolene, 0,7 wt% Joncryl also resulted in high stress at yield, an increase of 33 %, and pose an economical alternative. The increasing yield strength is a result of compatibilization, increased PP crystallinity and chain extension of the PET phase. A high degree of dispersion was obtained by high shear mixing which was a condition for obtaining high strength blends.

Compatibilizer Lotader, a ethylene-vinyl acetate-glycidyl methacrylate copolymer, did not compatibilize PP and PET blends well and combinations of Lotader and chain extenders resulted in poor mechanical properties. A glycidyl methacrylate grafted PP compatibilizer on the other hand would be of interest but is not available commercially.

Addition of 10 wt% glass fiber significantly increased the stress at yield and 0,4 wt% PBO addition increased it additionally.

The implication of the model system investigation is that recycling PP/PET blends can give materials with very good mechanical properties. Upgrading recycled polymers by reactive extrusion with compatibilizers and chain extenders was proven to be a successful and industrially applicable method.

7

Future work

The results from the model system show that upgrading of PP/PET blends by compatibilization and chain extension is a viable process. The recipes developed for the model system should thus be applied to the recycling of post-consumer PP/PET blends. This will be an important step in order to increase the production volume of materials made of recycled polymers.

For further evaluation of compatibilization and chain extension of PP/PET blends, a number of things can be additionally studied. A compatibilizer composed of glycidyl methacrylate grafted PP could be of high interest due to several studies reporting an increased compatibilizing capability compared to maleic anhydride grafted PP. Also, by varying the compatibilizer content about 1-2 % a more optimal compatibilizer concentration might be found. Optimization of the chain extender concentrations could also be investigated. In order to understand the connection between chain extenders and mechanical properties, more SEM images could have been taken to investigate the chain extenders effect on the microstructure. Furthermore, by measuring the intrinsic viscosity of the blends produced, better understanding of the degree of chain extension could be achieved.

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Appendix 1

A.1 Crystallization of PP and PET

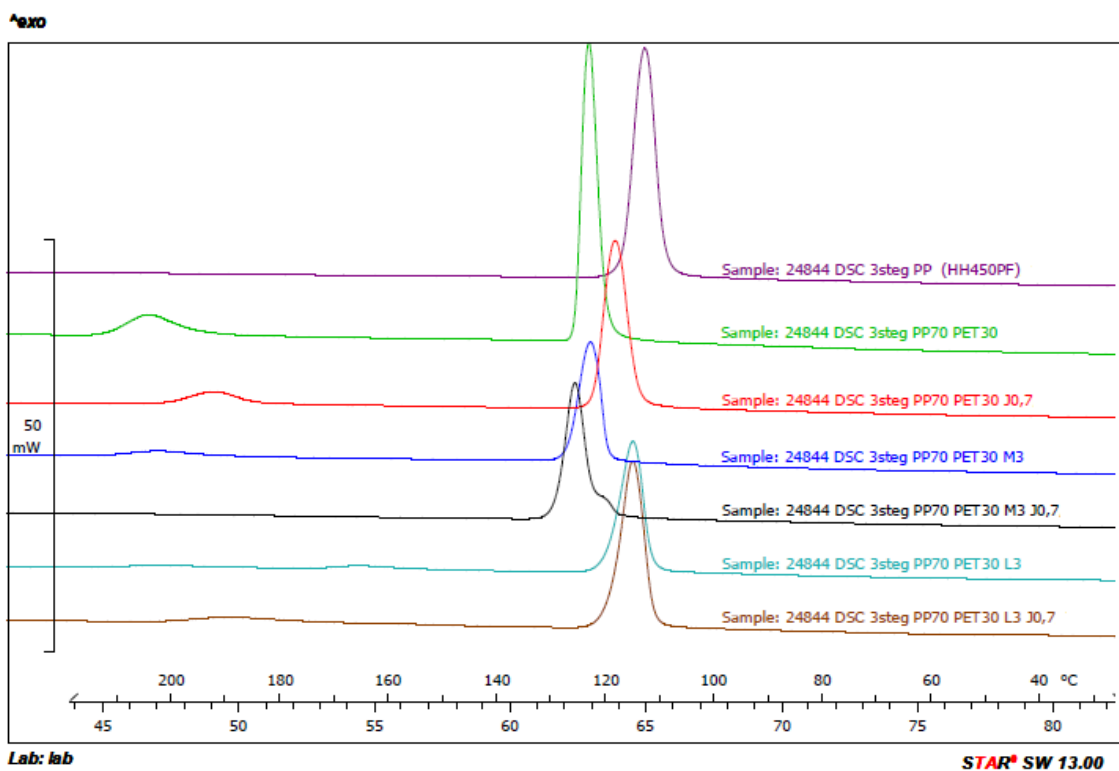


Figure A.1: Crystallisation behavior of blends with chain extender Joncryl.

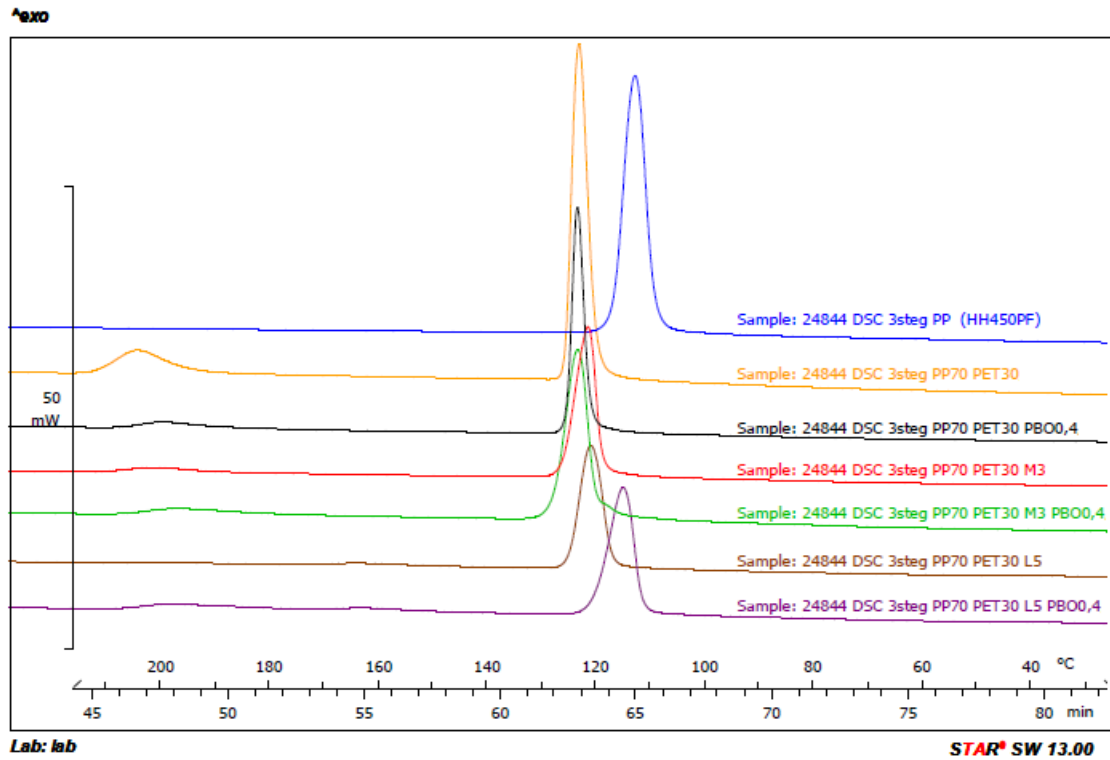


Figure A.2: Crystallisation behavior of blends with chain extender PBO.

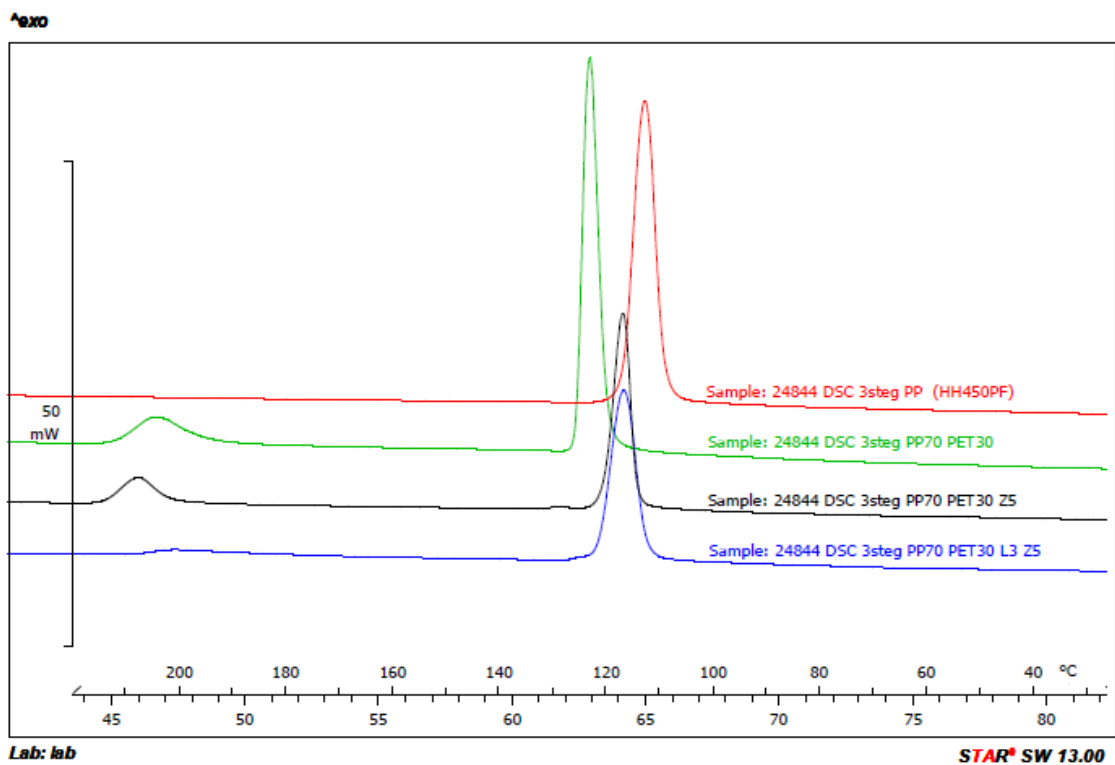


Figure A.3: Crystallisation behavior of blends with chain extender Zemac.

A.2 Crystallinity of PET

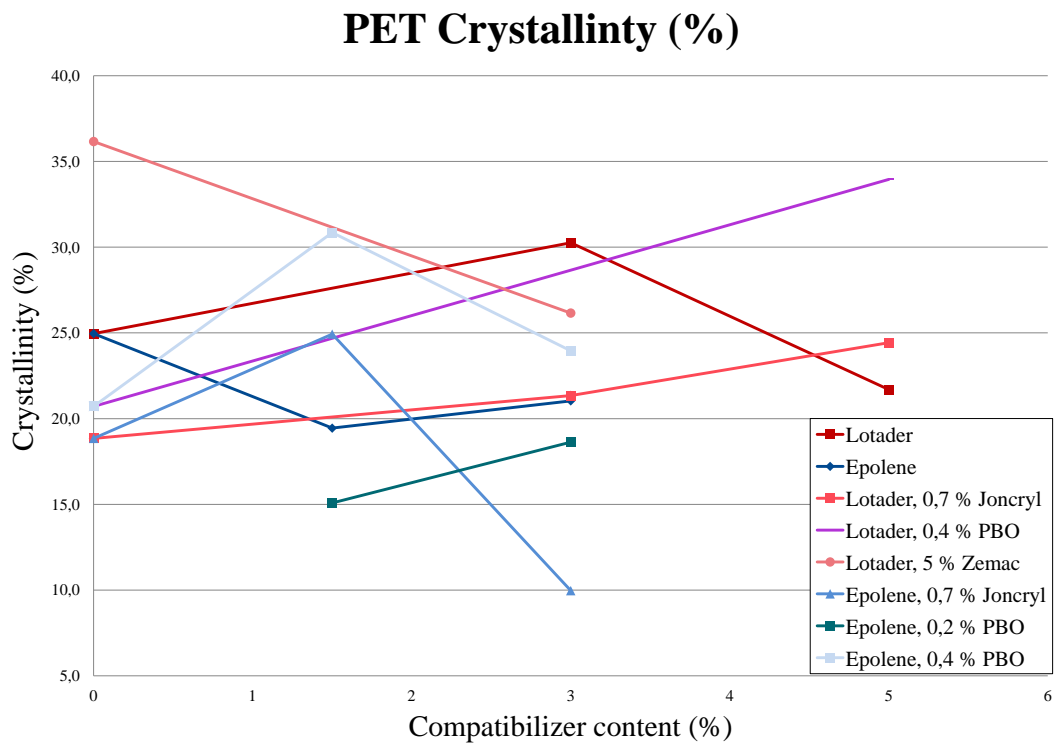


Figure A.4: The degree of crystallinity for the dispersed PET phase.

A.3 Impact strength

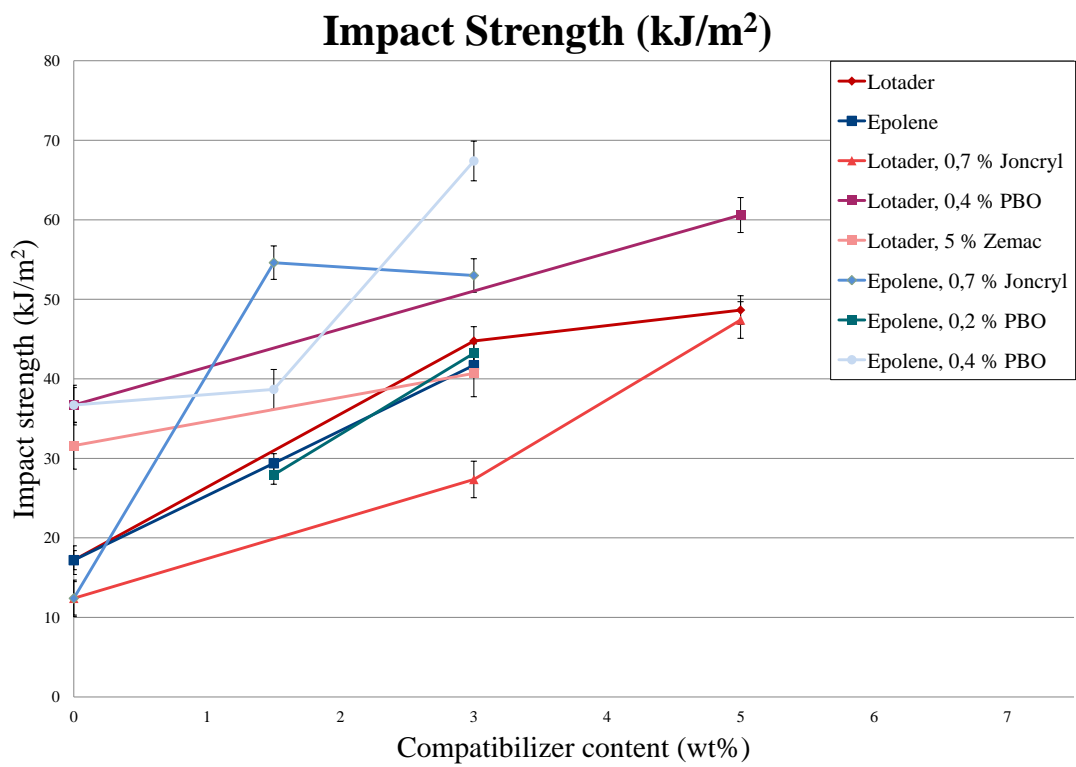


Figure A.5: Impact strength of un-notched blends with varying component compositions.