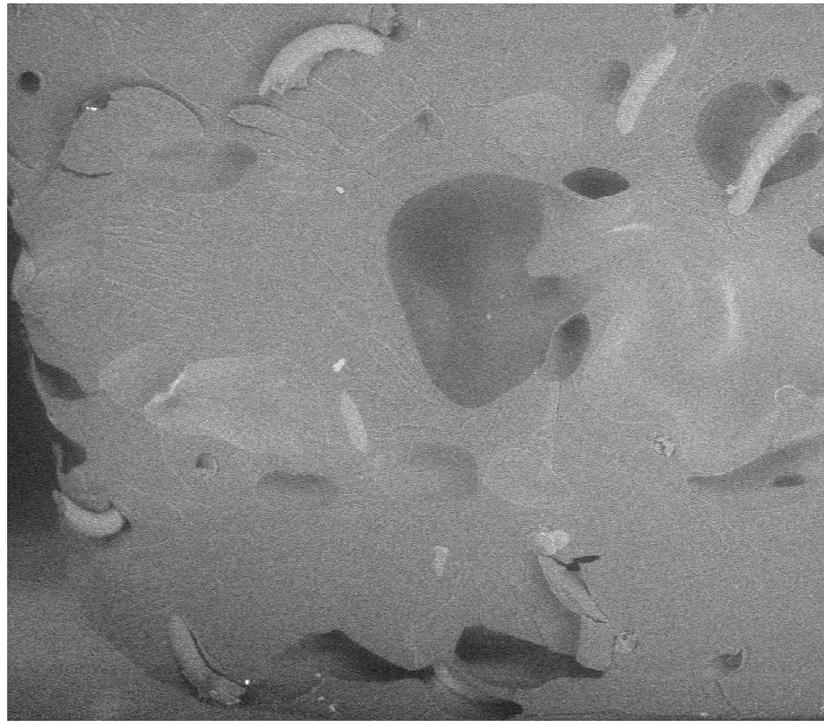


CHALMERS



Compounding of electrically conductive two phase polymer blends

Master of Science Thesis

ISABELL KINDGREN

Department of Chemical and Biological Engineering
Division of Applied Chemistry and Polymer technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2012
Report No. 409

REPORT NO. 409

Compounding of electrically conductive two phase
polymer blends

Isabell Kindgren

SUPERVISOR:

Martin Strååt, Swerea

EXAMINER:

Mats Andersson, Chalmers University of Technology

Department of Chemical and Biological Engineering
Division of Applied Chemistry and Polymer technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2012

Compounding of electrically conductive two phase polymer blends

ISABELL KINDGREN

© ISABELL KINDGREN, 2012.

Technical report no 409
Department of Chemical and Biological Engineering
Division of Applied Chemistry and Polymer technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone + 46 (0)31-772 3400

Cover: SEM image of LDPE matrix with PA6 fibers and MAPE compatibilizer

Teknologtryck
Göteborg, Sweden 2012

Compounding of electrically conductive two phase polymer blends

ISABELL KINDGREN

Department of Chemical and Biological Engineering
Division Applied Chemistry and Polymer technology
Chalmers University of Technology

ABSTRACT

One major problem in the plastics industry today is the poor recyclability of most plastics and especially composite products. In this study the electrical resistivity and mechanical properties of blends with recycled cross linked polyethylene (XLPE) or polyamide (PA) fibers in polyethylene or ethyl butyl acrylate were investigated. The XLPE material was granulated recycled high voltage XLPE cables from the cable industry. In the case of polyamide, fibers from the textile industry are utilized. Two types of carbon black were used. Method development for conductivity measurements and compounding of the composites was also looked into.

Maleic anhydride grafted polyethylene (MAPE), two random ter-polymers of ethylene, acrylic ester and maleic anhydride (PE-g-MA) and one random ter-polymer of ethylene, methyl acrylate and glycidyl methacrylate (PE-g-GMA) were investigated for their ability to compatibilize PA-fiber-PE-blends. The addition of compatibilizer did not in all cases improve the mechanical properties. The MAPE containing grade had the highest strain, followed by the PE-g-GMA. The fibers curl up during compounding, thus not adding to the mechanical properties to their full potential.

The possibility of forced interface percolation with polyamide fibers having conductive carbon suffused in the surface was assessed, but did not show significant increase of the electrical conductivity compared to the non-conductive fibers. Limited control over fiber size, size distribution and limited material quantity made the comparison difficult.

Forced double percolation was investigated with XLPE-PE blends. The degree of cross linking of the recycled material was important for both mechanical properties and electrical conductivity. Cross linked recycled PEX fillers increased the ductility and the electrical conductivity of HDPE-CB and LDPE-CB blends.

Keywords: Conductive polymer composite (CPC), Two Phase Blends, Carbon Black, Volume Resistivity, Percolation Threshold, Recycling, Mechanical Properties, Compatibilizer.

Table of contents

1. INTRODUCTION	6
2. THEORY	7
2.1 RECYCLING	7
2.2 PERCOLATION THEORY	7
2.3 CONDUCTIVITY IN POLYMER COMPOSITES	8
2.4 COMPOUNDING OF POLYMER COMPOSITES	9
2.5 COMPATIBILIZERS	10
3. MATERIALS AND METHOD	11
3.1 MATERIALS	11
3.2 COMPOUNDING	14
3.3 MATERIALS PRODUCED	15
3.4 COMPRESSION MOULDING	15
3.5 PREPARATION OF SAMPLES FOR CONDUCTIVITY MEASUREMENTS	15
3.6 CONDUCTIVITY MEASUREMENTS	16
3.7 MECHANICAL PROPERTIES	16
3.8 TGA AND DSC	17
3.9 SEM - EDX	17
3.10 EXTRACTION	17
4. RESULTS AND DISCUSSION	18
4.1. CONTACT RESISTANCE	18
4.2 INFLUENCE ON VR FROM COMPOUNDING AND SAMPLE PREPARATION METHOD	19
4.2.1 <i>Test specimen preparation method</i>	19
4.2.2 <i>Percolation thresholds</i>	22
4.2.3 <i>Brabender kneader compounding settings</i>	23
4.2.4 <i>Twin screw extrusion and. Brabender kneading</i>	24
4.2.5 <i>Twin screw extruder temperature profile</i>	25
4.3 FIBER FILLED BLENDS	26
4.3.1 <i>EBA – PA6 filled blends</i>	26
4.3.2 <i>LDPE - blends</i>	28
4.3.3 <i>Mechanical and electrical properties of compatibilized LDPE-PA6 blends</i>	30
4.4 PEX FILLED BLENDS	38
4.4.1 <i>DSC of PEX filled blends</i>	38
4.4.2 <i>Extraction of PEX and PEX filled blends</i>	39
4.4.3 <i>Conductivity of PEX filled blends</i>	40
4.4.4 <i>LDPE – PEX blends</i>	41
4.4.5 <i>HDPE-PEX blends</i>	42
5. CONCLUSIONS	43
6. FUTURE WORK	44
7. ACKNOWLEDGEMENTS	45
8. APPENDICES	45
REFERENCES	46
APPENDIX I	48

1. Introduction

One of the major problems in the plastics industry today is the poor recyclability of most plastics and especially composite products. High performance products are difficult to formulate from recycled material, particularly when considering the purity and compatibility which is closely coupled to the mechanical performance of the product. When using waste material from the industry, improved control of the content can be achieved and high performance polymer materials may be accomplished.

In this study, ethyl butyl acrylate (EBA), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), cross linked polyethylene (XLPE), poly amide 6 (PA6) and polyamide 6,6 (PA6,6) blends are examined with the intent of finding cheap materials with adequate mechanical and electrical properties that are possible to produce from recycled materials.

Polyethylene (PE) is common, cheap and relatively stable. XLPE is available from process scrap and recycled high voltage cables. Since XLPE is essentially polyethylene, the compatibility should be good. Polar polymer fractions such as PA6 may be incorporated in a PE matrix by means of a suitable compatibilizer. Fibers are geometrically suitable for reinforcement and PA6 fibers are readily available from the textile industry. Using fibers is also advantageous because the tensile strength of drawn PA6 fibers is 10 times as high as virgin polyamide [1]. Polyamide is also interesting due to the presence of reactive end and backbone groups, giving opportunity for reactive compatibilization [2].

Electrically conductive composites have many uses, including antistatic applications, electromagnetic shielding and self regulated heating [3]. In order to create electrically conductive composites, carbon black (CB) is often added. Carbon black often contains oxygen containing species in the surface, making the surface slightly polar. Since PA6 is more polar than PE, there may be some transport of CB in the melt from the polyethylene to the PE-PA6 interface, possibly generating interface percolation.

Compounding at lower temperature than the melting temperature of PA6 or using XLPE will give rise to forced double percolation. The carbon black may not enter the crystalline solid phase of the PA6 and not the cross linked XLPE network, thus allowing maintained electrical conductivity with lower concentration of CB per amount of final material. PA6,6 fibers with conductive carbon suffused into the surface (~1 μm) are available commercially. If such fibers are melt mixed into the polyethylene matrix below the PA6,6 melting point, it may be possible to achieve a fiber reinforced PE with a super low percolation threshold by forced localization of CB in the interface.

2. Theory

2.1 Recycling

Recycling of polymers and especially polymer blends and composites is a complex issue. The major problem is that the majority of recyclable (thermoplastic) materials are mixed, i.e. there are several types of polymers and other products in the same feed. Sorting it thoroughly would in many cases not be profitable.

When using scrap from the industry (as opposed to domestic), improved control of the composition may be achieved, thus allowing for higher quality end products. Immiscible blends may be desirable in the context of reinforcement and conductivity. In order to generate sufficient mechanical properties compatibilizers must be added. Given the right compatibilizer, the blend may have properties superior to the virgin polymers.

A two phase polymer blend may exhibit lower percolation threshold (low resistivity with low filler concentration) through exclusion effects or give rise to double percolation. Incorporating a softer material into a hard but brittle matrix may also improve the ductility and thus mechanical properties such as elongation and impact strength [4].

2.2 Percolation theory

The electrical properties of conductive polymer composites (CPCs) are very different from those of homogeneous conductive materials such as pure metals. In low enough loadings of conductive filler, the resistivity (R) of the CPC will not differ much from that of the pure matrix. However, at some level of filler concentration, the resistivity may drop several orders of magnitude, i.e. the material percolates.

The theory of electric conductivity in electrically conductive composites has been evaluated, among others, by Weber et al. [5]. Predictions about electrical performance of a CPC have proven to be very difficult and depend greatly on experimentally determined factors. One of the major models used in this area is the percolation theory. It originated in the field of fluid dynamics and is used as a statistical model in several different fields including material science, disease- and fire spreading [6, 7].

Percolation theory compares the composite to a lattice with edges or nodes which are either open or closed with some probability P . If enough nodes are open, an open path is created throughout the whole lattice. This open path that is created may be interpreted as the percolation threshold and is seen in the CPC as a sudden drop in resistivity with increased filler concentration. Thus, when enough conductive particles introduced in the CPC are close enough to each other to allow tunneling of electrons, or connect, a conductive path is created. This is schematically illustrated in Figure 1, on the left.

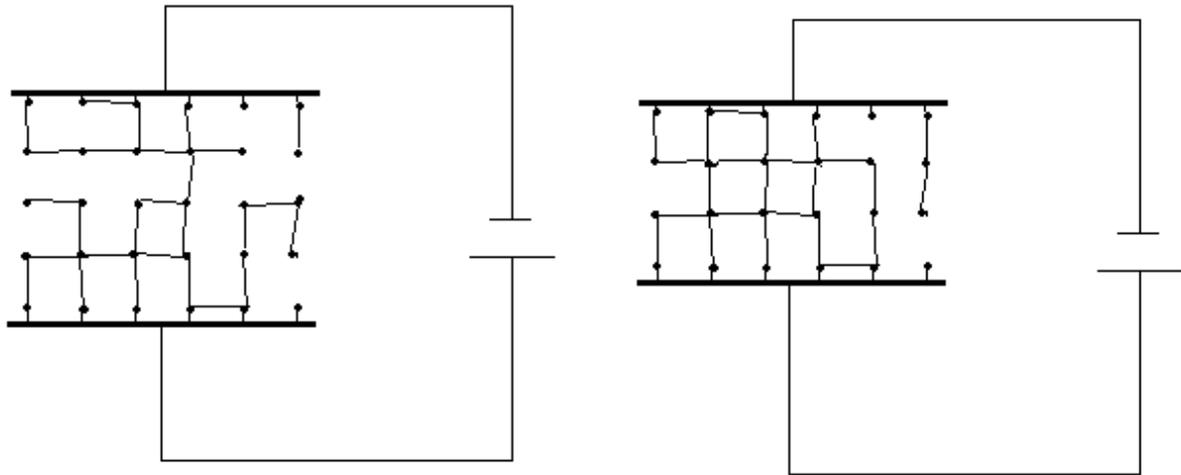


Figure 1 - Illustration of percolation theory applied on disordered electrical networks, full volume on the left, reduced volume on the right. Image created with inspiration from Grimmett [7]

One interesting approach is that of double percolation. Double percolation is the percolation of two polymer phases and the percolation of carbon black combined. The distribution of the polymer phases is crucial. The carbon black may selectively go to one of the phases and if that phase is continuous throughout the matrix, double percolation is achieved.

This may be compared to the addition of insoluble filler where no CB may penetrate. The dilution of the material may be interpreted as decreased resistivity per volume of material without extra addition of CB [7]. The effective concentration of CB increases. When the volume where the CB may be distributed decreases, an increased number of conductive pathways may be facilitated. This is illustrated in Figure 1 on the right.

Double percolation strategy is a tool in the combat against the problems with reduced mechanical properties in high filler loadings. There are however several key issues when mixing two polymers into one composite, the adhesion between the two immiscible polymer phases being the most central. It is imperative to choose a suitable compatibilizer or by other means ensure good adhesion between the phases, without obstructing the conductive network.

2.3 Conductivity in polymer composites

A common filler used to increase electrical conductivity of polymer blends is carbon black. There are many kinds of carbon black available on the market today with different production methods, surface area, aggregate shape, pH, price, and percolation threshold. The size and shape of the aggregates of CB are crucial for the percolation threshold. The four main groups of aggregate shapes are spheroidal, ellipsoidal, linear and branched, where the high structure and high surface area CBs such as the branched variety generally achieves the lowest percolation threshold, but are also generally more expensive. Several other kinds of conductive fillers are also used to facilitate conductivity in an otherwise insulating matrix, such as metal particles, carbon nanotubes and exfoliated graphite [8].

Filler concentration at the percolation threshold can range from 1-62% wt in the same matrix depending on the type of CB [8]. For spherical particles the percolation threshold is 16%. Generally the more filler is added, the lower the resistivity, while the mechanical properties degenerate with higher filler concentration. In order to reduce the cost and improve processing and mechanical properties, a low amount of filler is desired. To facilitate a combination of good electrical and mechanical performance the filler type and concentration must be well chosen.

Selective localization of CB at the polyblend interface is very efficient, if achieved, to reduce the percolation threshold. This scenario would be possible if the carbon black was transported by a favorable driving force towards one of the phases, but not entering that phase. The transport rate in the media and the driving force must be sufficient at the same time as the preferred phase is impenetrable or the transport rate is much higher in that phase. It may also be achieved by forcing CB to stay at the interface by physical means, such as reported by Gubbels et al [9], where two powdered polymer components were dry mixed together with CB and subsequently compression moulded. The shear forces in the compression moulding are very low and the processing time is relatively short. Thus the CB may not migrate from the particle interface, giving rise to the extremely low percolation threshold of 0,4%wt. The mechanical properties were however poor [9].

In this study, forced double percolation by physical means is investigated. The CB cannot enter the XLPE due to the cross linking and it cannot enter the PA-fibers due to the fact that it is not molten during compounding. Forced interfacial double percolation may be achieved by using carbon treated fibers.

2.4 Compounding of polymer composites

The distribution of the filler and thus the conductivity of the material largely depend on the production method. A quick and easy way to compound small amounts of many different composites is the batch wise internal kneading mixer. Two counter rotating kneaders rotate within a chamber and a fixed volume of polymer and additive is inserted. The polymer is molten and sheared within the chamber to distribute and disperse the filler. After a desired time period, the material is removed from the chamber.

The other method used in this study is the continuous twin screw extruder. The screw needs to be designed to fit the polymer blend of interest. Different sectors of the screw such as feeding, compression and mixing zones are combined in a certain order to achieve good mixing [10].

2.5 Compatibilizers

In order to facilitate good adhesion between immiscible polymers in a composite, a compatibilizer needs to be introduced. The choice of compatibilizer is crucial to the mechanical performance.

A strong interaction or chemical bonds to the NH group in the nylon chain may be achieved with glycidyl methacrylate (GMA) or maleic anhydride (MA) [2, 11]. The compatibilization of PE-PA6 blends has been readily studied by E.G.Koulouri et al [2]. Ethylene-glycidyl methacrylate copolymer (PE-g-GMA) is used in the study for in situ formation of copolymer in an interfacial reaction. Promising mechanical results were presented and reaction between the compatibilizer and the PA6 was concluded to have taken place. The study by Jiang et al [11] investigates the reactive compatibilization of LDPE/PA6 blends with maleic anhydride grafted polyethylenes (PE-g-MA). The reactivity of the maleic anhydride towards the PA6 is concluded to be sufficient. In this study, both PE-g-GMA and PE-g-MA compatibilizers are investigated.

Another conclusion made by Jiang et al [11] is that the solubility of the compatibilizer in PE should not be too great. This would readily distribute the compatibilizer in the PE-matrix and the concentration of compatibilizer at the polyblend interface would be low. To achieve good compatibilization between PA and LDPE it is thus preferred to have good reactivity towards the amide and an intermediate solubility of the grafted polymer. For this purpose, compatibilizers with different polymer grafts, one aliphatic and three more or less polar copolymers are used.

3. Materials and Method

3.1 Materials

The Ethylene- Butyl Acrylate (EBA) used was LOTRYL 17 BA 07, from Arkema, France, random copolymer, butyl acrylate content 16-19% wt, MFI (2,16 kg / 190 °C) 6,5 – 8,9 g/10min, density 930 kg/m³, melting point 89 °C. All material information was obtained from the supplier. Generic structure is shown in Figure 2.

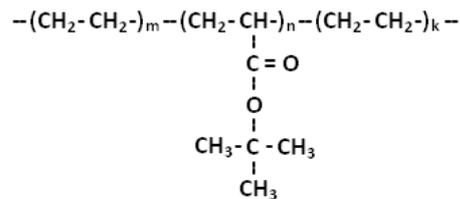


Figure 2 - Generic structure of EBA, image created with information from supplier [12]

The Linear Low Density Polyethylene (LLDPE) was Aspun 6835 A, from Dow Chemical Company, Belgium, MFI (2,16 kg / 190 °C) 17 g/10 min, melting point 129 °C, density 950 kg/m³. All material information was obtained from the supplier.

The Polybutylene terephthalate (PBT) was Ultraform® H2320 006, from BASF, MFI (2.16kg/190°C) 4,1 g/10min, density 1400 kg/m³. All material information was obtained from the supplier.

The low density polyethylene (LDPE) was supplied by Borealis AB, MFI (2,16 kg / 190 °C) 2 g/10 min. The material information was obtained from the supplier.

High density polyethylene (HDPE), grade MG9601 from Borealis, MFI (2,16 kg / 190 °C) 8 g/10 min, density 964 kg/m³. This material is designed for injection moulding of rigid products with high impact strength and good flow properties. All material information was obtained from the supplier.

Polyamide 6 (PA6) fibers for flocking, 75 µm diameter, cut in 2 mm length were utilized, generic formula available in Figure 3. A portion of the fibers were washed in ethanol in order to remove processing additives.

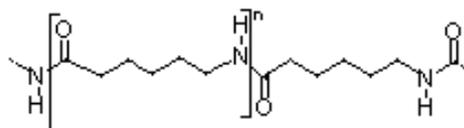


Figure 3 - Polyamide 6 generic formula

Table 1 - Properties of the different grades of Lotader

Grade name	Lotader 3210	Lotader 3410	Lotader AX8900
Composition	Random ter-polymer of ethylene, acrylic ester and maleic anhydride	Random ter-polymer of ethylene, acrylic ester and maleic anhydride,	Random ter-polymer of ethylene, methyl acrylate and glycidyl methacrylate
Reactive specie content	Maleic anhydride 3,1% wt	Maleic anhydride 3,1% wt	Glycidyl methacrylate 8% wt
Co-monomer conc.	Butyl Acrylate 6% wt	Butyl Acrylate 17% wt	Methyl Acrylate 24% wt
Processing temperature	From 270 °C 320 – 330 °C	From 270 °C 320 – 330 °C	-
Melt index, 2,16 kg @ 190°C	5 g/10min	5 g/10min	6 g/10min
Density	0,94 g/cm ³	0,94 g/cm ³	0,94 g/cm ³
Melting point	107 °C	89 °C	65 °C

Several batches of cable production waste were used in this study. All recycled material was obtained from high voltage cables (HVC). All recycled batches may contain small traces of copper, aluminum and various thermoplastics from the cable recycling process. The known material characteristics are summarized in Table 2.

Table 2 - PEX HVC waste material from the cable industry

Material name	Origin	Main Material composition	Grain size (maximum)
SWE05	Cable scrap	Peroxide cross linked polyethylene	0,6mm
SWE12	Cable scrap	Peroxide cross linked polyethylene	0,6mm
SWE14	(50%) Cable manufacturing scrap and (50%) end-of-use cables	Peroxide cross linked polyethylene	0,6mm
S 5	Lumps from cable production	Peroxide containing polyethylene	0,6mm

The carbon black grade called CB1 was Ketjenblack EC 600JD from AKZO NOBEL, the Netherlands, with aggregate size 10–50 nm, apparent bulk density 100–120 kg/m³, BET surface area 1250 m²/g, pore volume 480–510 cm³/100 g, and pH 8–10. All material characteristic data were provided by the supplier.

A second carbon black grade, called CB2, was Ensaco 250 P from Timcal, Switzerland, bulk density 200 kg/m³, particle size 45 µm, BET surface area 62 m²/g and pH 10. All material characteristic data were provided by the supplier.

3.2 Compounding

The carbon black and polyamide fibers were dried in a vacuum oven at 80 °C for 16 hours before use. All materials were otherwise used as received, if nothing else stated.

The polymer blends in this study were compounded by melt mixing in a kneading mixer with a chamber volume of 30 cm³ (Brabender AEV 651) or a twin screw extruder (Coperion, ZSK 26K, 10.6, 2009) with 10 heating zones.

The materials compounded in the kneading mixer were produced according to temperatures and settings in Appendix I, Table 1 and the materials produced with the twin screw extruder were produced according to conditions in Appendix I Table 2.

3.3 Materials produced

The composition of all the materials produced in this study is available in Appendix I Table 3, and the mixing methods are given in Appendix I, Table 1 and Table 2.

3.4 Compression moulding

Plaques were compression moulded in three different hot presses. One hot press with controlled cooling was built in-house (press 1). The second hot press used was (J. Wickert & Söhne) without cooling (press 2). The third hot press was (Collin) P300M (press 3) with controlled cooling. Compression moulding conditions are available in Table 3.

Table 3 - Compression moulding settings, starting and holding temperature were the compounding temperature regarding each material according to Appendix I, table 1 and 2.

Press	Holding time	Press type	Cooling rate	Cooling pressure	Plaque thickness
Press 1	1 min	Positive mould	15°C/min	Unknown	1 mm
Press 2	1 min	Frame	Unknown	None	1 mm
Press 3	3 min	Frame	15°C/min	200 bar	2 mm

3.5 Preparation of samples for conductivity measurements

Strings were prepared by extrusion with a capillary rheometer Rheoscope 1000 (CEAST, 6742/000), 10 mm/min extrusion speed. The temperatures in both compression moulding and extrusion were the same as the compounding temperature for each compound, see Appendix I Table 1, 2 and 3.

Two different dies were used for the extrusion, one with an opening of 1 mm in diameter, length 10 mm. The other die had a 2 mm diameter opening and a length of 8 mm. The strings were cut with a razor into suitable lengths, 20 – 100 mm. The plaques were cut with scissors into pieces 3 – 10 mm width and 20 – 100 mm length. Silver paint Dottie Electroconductives (Fujikura Kasei Co Ltd) was used to reduce contact resistance.

3.6 Conductivity measurements

The resistivity of the samples was measured with two or four point probes. The four point probe (4p) measurements were conducted with a precision multimeter (Fluke 8846A) by connecting the samples according to Figure 7. This method is automatic and the equipment applies a voltage over the sample enough to generate a current of 0,01 mA, and measures the resistance.

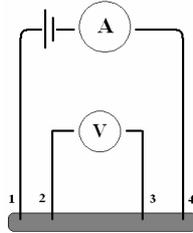


Figure 7 - Four point probe conductivity measurement

In the case of the two point probe (2p) method, a power supply (Oltronix) applied a voltage (U) over the samples. The voltage (varied between 1 and 100 V) was measured by a multimeter (Fluke III true rms). The current (I) was measured by a precision multimeter (Fluke 8846A). The volume resistivity (ρ) was calculated according to Eq.1

$$\rho = \frac{UA}{IL}$$

Eq. 1 – Volume Resistivity

Where L is the measured sample length (cm), A is the area of the cross section of the sample (cm^2), U is the measured voltage (V), I is the current (A) and ρ is the volume resistivity (Ohmcm). The conductivity of the sample σ (s/cm) may be calculated according to Eq.2.

$$\sigma = \frac{1}{\rho}$$

Eq. 2 - Conductivity

3.7 Mechanical properties

A cutting die according to ISO527-2 5A was used to produce dumb bells. A tensile testing equipment (Hounsfield H5KT 0112) with a 1kN load cell, was used to determine max stress (%) and strain (MPa).

3.8 TGA and DSC

Materials were investigated with a thermo gravitational analyzer (TGA) (TGA/DSC1, Mettler Toledo, STAR^e System), and a differential scanning calorimeter (DSC) (DSC1 Mettler Toledo, STAR^e System). The TGA method used was according to Table 4 and the DSC method according to Table 5.

Table 4 - TGA method

Stage	Stage 1	Stage 2	Stage 3	Stage 4
Temperature interval	50-600°C	600°C	600-900°C	900-50°C
Time	27.5 min	40 min	15 min	45min
Heating rate	20 °/min	fixed	20 °/min	- 20 °/min
Media	N ₂ 50 ml/min	Air 50 ml/min	Air 50 ml/min	Air 50 ml/min

Table 5 - DSC method

Stage	Stage 1	Stage 2	Stage 3
Temperature interval	30-260 °C	260-30 °C	30-260° C
Heating rate	10 °C/min	-5 °C/min	10 °C/min
Media	N ₂ 80 ml/min	N ₂ 80 ml/min	N ₂ 80 ml/min

3.9 SEM - EDX

A scanning electron microscope (SEM) from Jeol (JSM -6610 LV) was used to obtain images of composite microstructure. Samples were cryofractured in liquid nitrogen prior to imaging. Energy-dispersive X-ray spectroscopy (EDX) was used to identify contaminants.

3.10 Extraction

Extraction was performed in boiling decahydronaphtalene (decalin) for 7+1 h in order to remove all non-cross linked polyethylene. Extraction experiments were conducted in accordance with ASTM D 2765:2001, with the exceptions that the antioxidant level was 0,05%, and extraction was performed for one extra hour with new solvent without antioxidant. This is in accordance with an internal method at Borealis AB Stenungsund. All powder samples were sifted in a 355 µm sieve before extraction.

4. Results and discussion

4.1. Contact resistance

Contact resistance is a problem that often arises when measuring the resistive properties of materials, particularly in conductive polymer composites. It generally manifests itself so that the measured volume resistivity (VR) of a material changes with the applied voltage; generally a reduction in resistivity with increasing voltage.

The results of four different approaches to this problem can be found in Figure 8. It is clear that sanding the material *increases* the contact resistance. It is also evident that using silver paint and four-point probes gives the lowest (and most accurate) resistivity values.

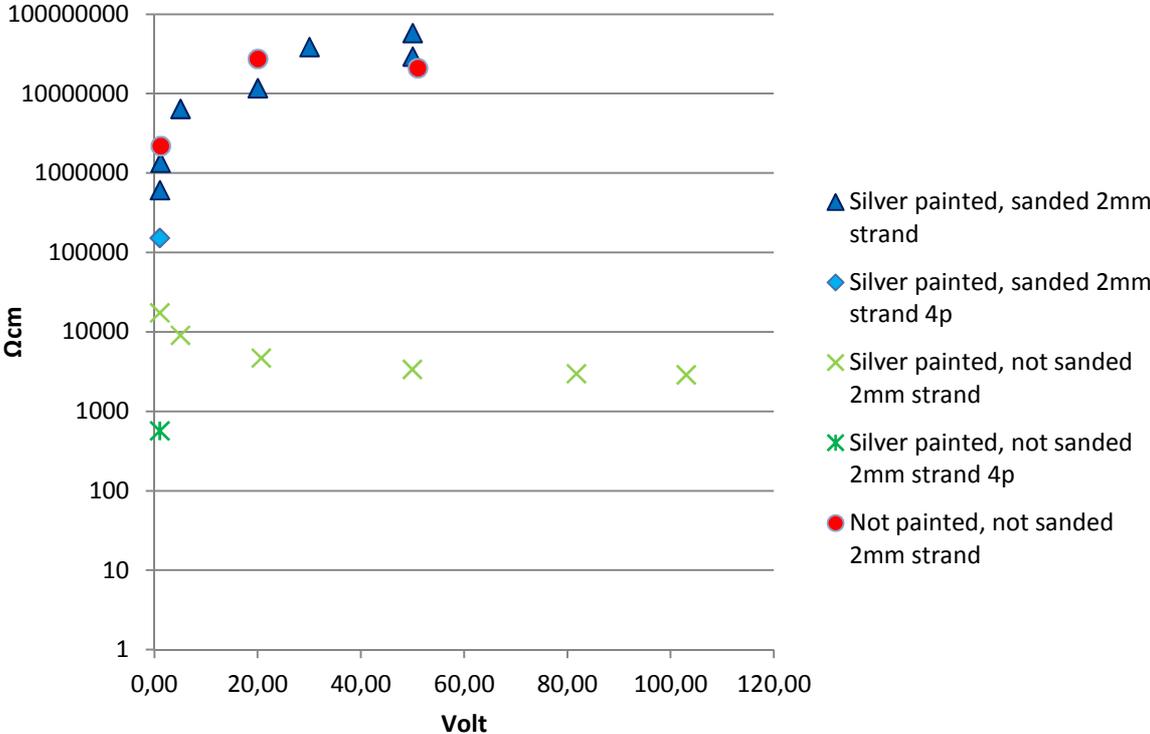


Figure 8 - The influence of sanding and silver paint on the contact resistance in samples of EBA 1 which contained 5% wt CB, 2mm strands, VR measured with two and four point (4p) probes, measurement with four point probes was not possible for the not painted, not sanded specimen since it was outside the equipment range

As seen in Figure 8, the volume resistance in some samples changed with increased voltage which indicated that the contact resistance was considerable. All samples were made from the same batch (EBA 1) using the same preparation method. Without any treatment of the sample specimen, the contact resistance was very high (red dots). A known method to reduce the contact resistance is to apply silver paint. This was confirmed to give a significant effect and reduced the contact resistance (green X 2p, green star 4p).

Careful sanding of the sample was carried out in order to remove a possible layer of non conducting material in the surface. However, the sanding did not reduce the contact resistance (blue triangles 2p, and diamond 4p). The volume resistivity of the both sanded and silver painted strand was in the same region as the untreated sample.

It is possible that the silver paint did not wet the sanded surface, leaving air in pockets between the strand and the silver paint which is illustrated schematically in Figure 9.



Figure 9 – Schematic cross section of the silver paint wetting of sanded (left) and non sanded (right) strands.

4.2 Influence on VR from compounding and sample preparation method

It is well known that the processing properties of the material determine the conductivity to a large extent [10]. The compounding *conditions* during mixing of the composite are crucial to its performance. Increased temperature will reduce the viscosity of a polymer, which will facilitate distribution of i.e. CB in a composite. However, the agglomerates of CB particles needs sufficient shear to break up, hence lower temperature and thus higher viscosity would improve the dispersion.

It has been shown by G. Kasaliwal et al. [14] that increasing the shear stress by increasing screw speed and reducing the temperature can break up agglomerates and reduce VR of CPCs. The same study has shown differences in resistivity depending on sample preparation as large as 14 orders of magnitude [14].

4.2.1 Test specimen preparation method

A minor trial was conducted to estimate the extent of the difference between different test specimen preparation techniques. Four methods were investigated, strings extruded through two different dies and compression moulded plaques with slow and fast cooling. In Figure 10 it can be observed how the different preparation techniques influence the volume resistivity of EBA1.

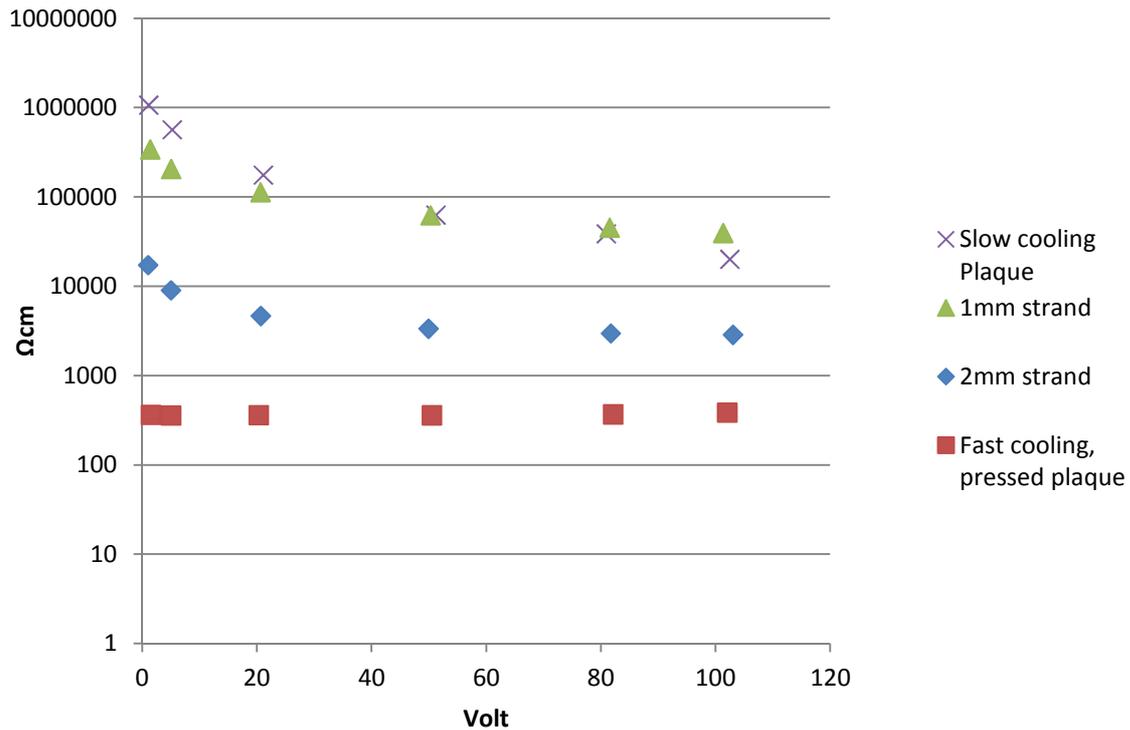


Figure 10 - Test specimen preparation method dependence on the volume resistivity of EBA 1 (5% wt CB1), average from two samples, two point probes were used to measure VR

The variation between the different sample preparation techniques was considerable. However, contact resistance problems remained, as the resistivity tended to decrease with increased voltage.

The plaque with slow cooling and the string extruded through the smaller die generated the highest values of resistivity. The method that generated the lowest VR and which also from a lab perspective was the fastest and easiest to prepare was plaques with fast cooling. The VR of the 2 mm strand was somewhere in-between. The majority of the EBA samples were thereafter produced with plaques with fast cooling.

This conclusion was however not valid for the other materials tested, especially when considering the LLDPE and PBT samples. Figure 11 illustrates the differences in VR depending on sample preparation.

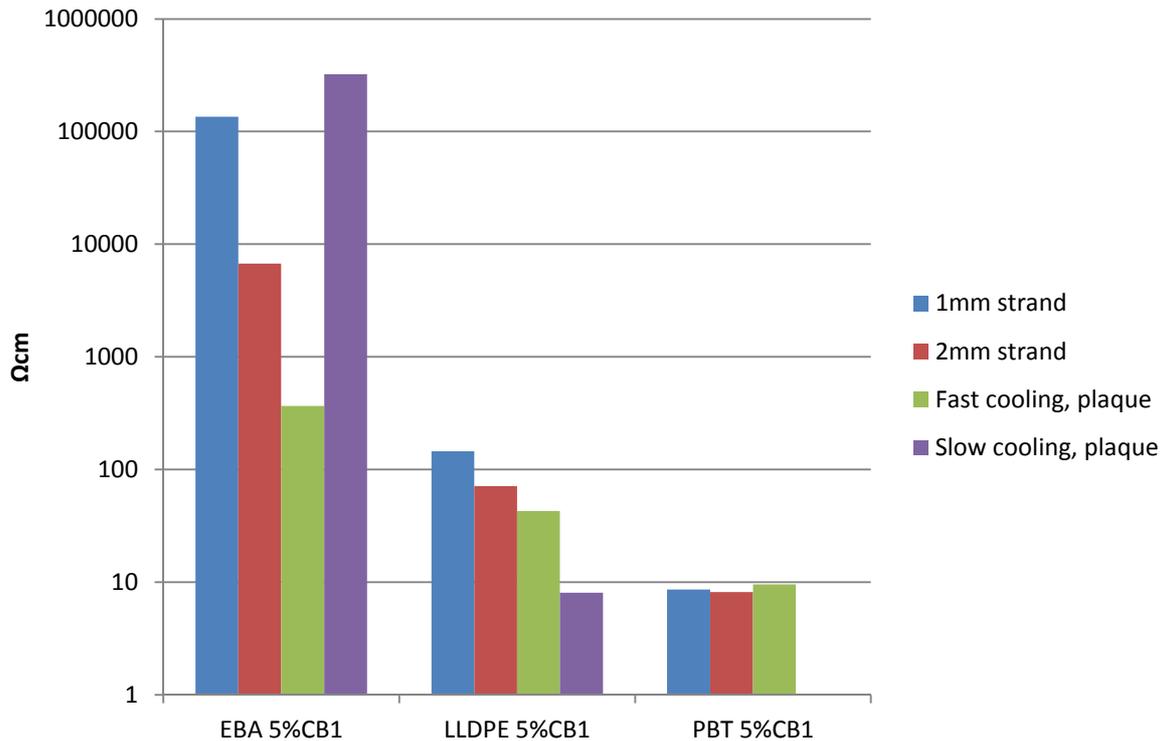


Figure 11 - Volume resistivity dependence on test specimen preparation method on the of EBA1 (EBA 5% wt CB1), PE15 (LLDPE 5% wt CB1) and PBT 1 (PBT 5% wt CB1), average of two samples, VR measured between 1-80V, four preparation techniques were tested for EBA and LLDPE and three techniques for PBT

In the case of LLDPE, strands obtained from the small die had the highest VR, similar to the case with EBA. However, the lowest resistivity value was achieved with plaques produced using slow cooling, contrary to the behavior of EBA. The LLDPE plaque produced with fast cooling performs at the same level as the strands, which were also cooled fast. The 1 mm strands naturally cooled faster than the 2 mm strands, also generating higher VR.

This difference in behavior compared to EBA is not particularly strange when considering the mechanism of conduction and its dependence on a favorable microstructure. Extrusion rate, die pressure and thus die swell, moulding pressure, holding pressure and cooling rate are factors that influence the microstructure. A lower percolation threshold may be obtained in semi crystalline polymers due to the fact that crystal regions reject CB particles, enriching the amorphous phase [15]. Cooling rate is particularly important in deciding the size, shape and degree of crystallinity which significantly affects the conductivity of a CPC. If the cooling is too fast, crystallites do not have time to form, increasing the amorphous part of the matrix.

Since LLDPE is much more crystalline than EBA, the cooling rate becomes a more important parameter for LLDPE. EBA does not require slow cooling since it is largely amorphous due to its structure and cannot form many crystallites. The plaques with slow cooling were chosen for subsequent trials with LDPE.

The difference between the highest and lowest VR of EBA is almost four orders of magnitude, while the PE results are spread within two. It is obvious that all materials are not

equally sensitive to the preparation method. The VR of PBT cannot be said to differ significantly depending on the preparation method.

4.2.2 Percolation thresholds

The variation in sensitivity towards specimen preparation method may also be an effect of how close the compounds are to their percolation threshold. The closer the material is to its percolation threshold, the larger the effect on VR, even from small changes in microstructure.

Also, the speed of crystallization will affect the results, where a material with a faster crystallization process will depend less on the cooling speed and vice versa.

In Figure 12 EBA and LLDPE with different concentrations of CB1 were compounded in the Brabender kneader and VR was measured.

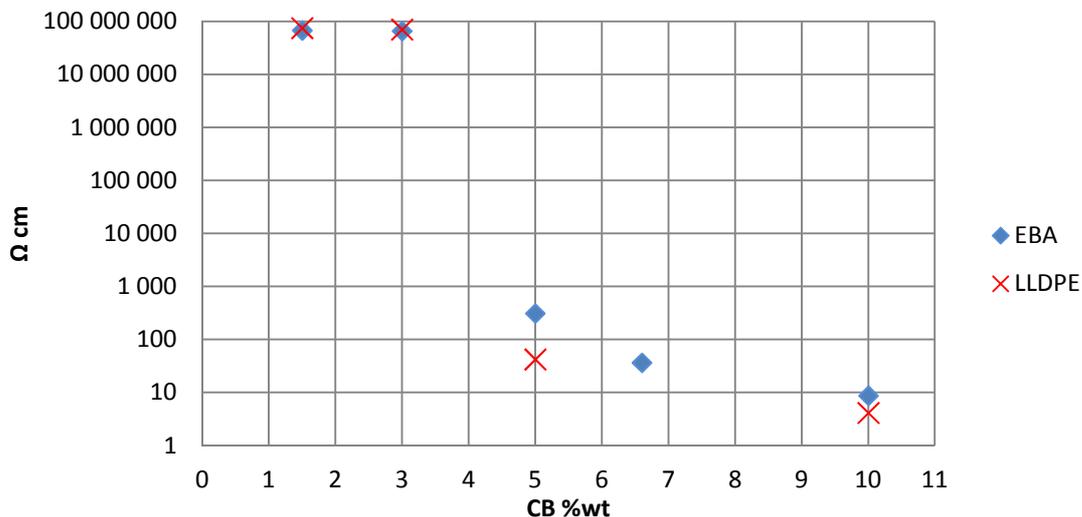


Figure 12 - Volume resistivity of EBA and LLDPE compounded in Brabender kneader with different CB1 concentrations (materials EBA1&5-8 and PE13-16, see Tabl), average data from two samples, two point probe measurements at 20V

The data was not extensive enough to establish a true percolation threshold for either of the materials. However, when the data at 5% wt was considered, the EBA had one order of magnitude higher VR than PE and both samples have similar VR at 3% wt.

This could indicate that EBA has a higher percolation threshold than the LLDPE. Thus the EBA1 samples in the specimen preparation study may have been closer to its percolation threshold than the LLDPE, generating more varied VR results depending on the specimen preparation.

4.2.3 Brabender kneader compounding settings

In order to study the influence of mixing on the volume resistivity of the final product, batches of PE and EBA were compounded using different screw speeds and temperatures. Compounding procedures corresponding to Mix2 and Mix4, (see Appendix I, table 1) were used. The results in Figure 13 are all measured on plaques moulded with fast cooling and all samples contained 5% wt of CB1.

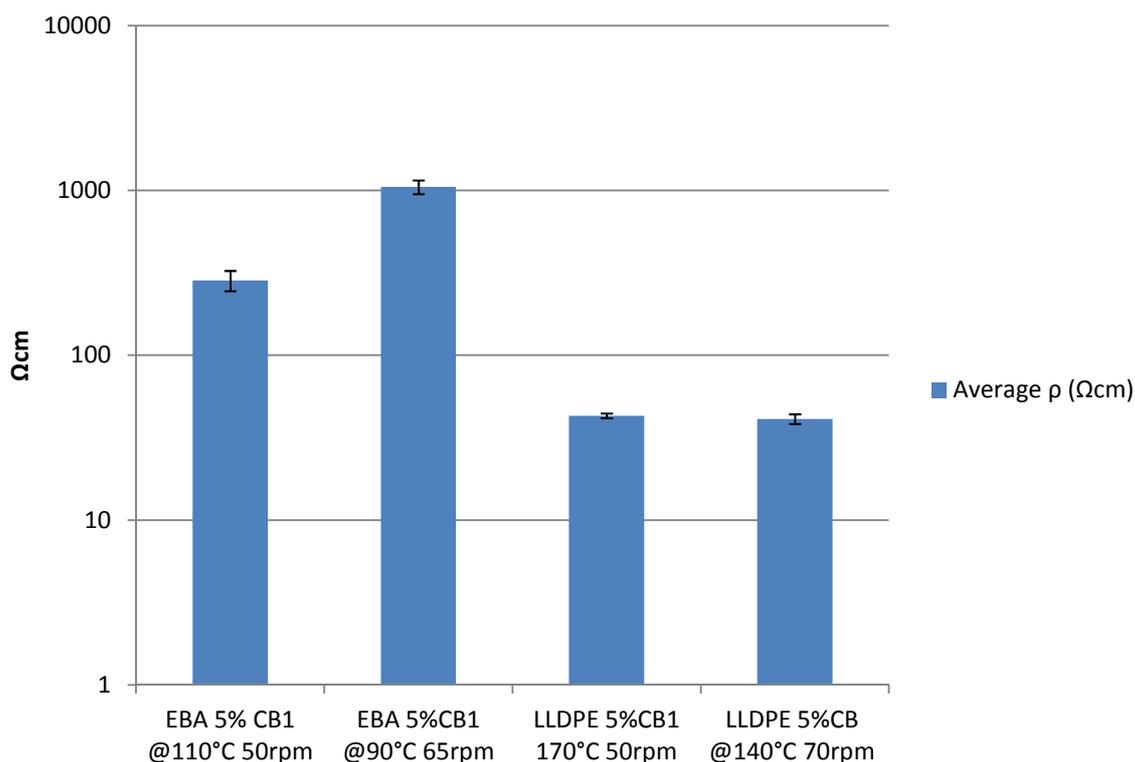


Figure 13 – Influence of mixing procedure on volume resistivity on materials EBA 1, EBA 9, PE 15 and PE 17, compounding temperature and screw speed noted on each sample, CB level held constant

There was no significant difference between the two PE grades, while the EBA showed a higher resistance after compounding at lower temperature and higher shear. Due to issues with the machine max torque, higher screw speeds were not investigated.

It is possible that the CB agglomerates were not ground to any finer particles because the difference in screw speed was not large enough while the EBA wets the CB more efficiently at higher temperature and thus facilitates distribution of the CB.

The LLDPE results may be interpreted similarly, but the material may have been further from its percolation threshold than EBA, thus not showing any large differences in VR.

4.2.4 Twin screw extrusion and. Brabender kneading

As well as the settings, the compounding method will affect the CB distribution and dispersion, hence also the resistivity of the CPC [8]. In Figure 14 the difference in VR of the material between the twin screw extruder and the Brabender internal kneading mixer is illustrated. LLDPE and CB1 were mixed in different amounts with the twin screw extruder and the kneader.

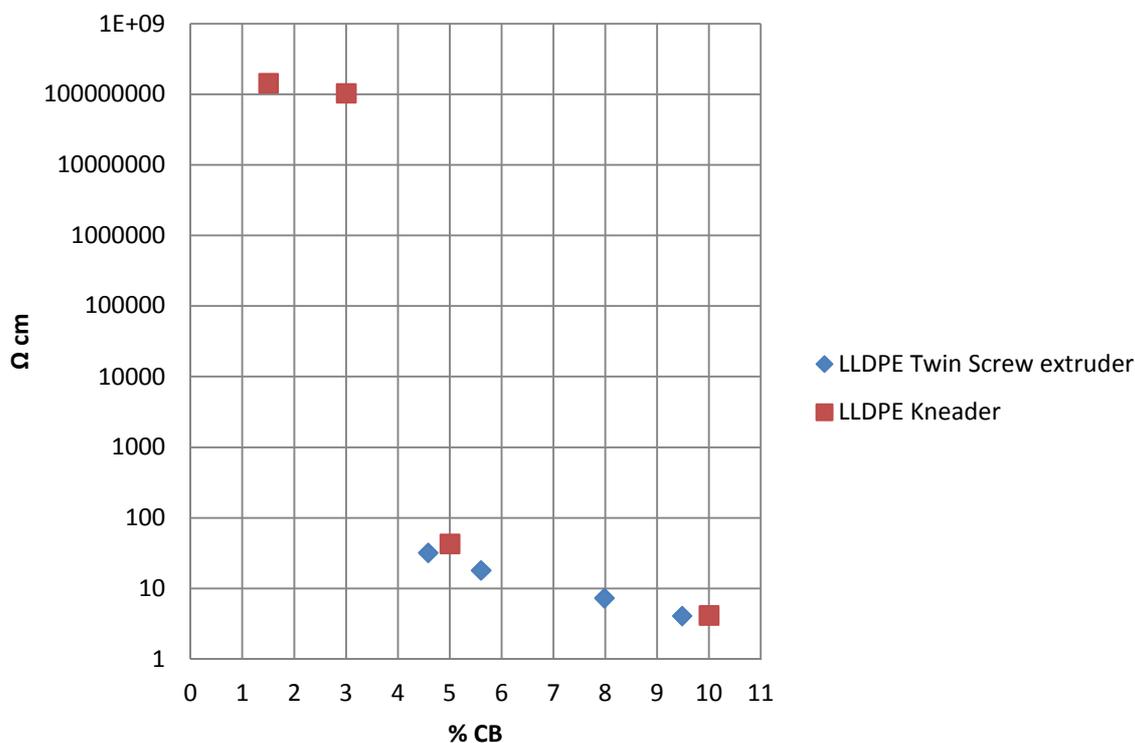


Figure 14 – Resistivity vs. CB concentration for LLDPE materials (PE 1 and PE 9-16) compounded with twin screw extruder or Brabender kneader, CB content determined with TGA for materials produced with twin screw extruder (PE 1 and PE 9-12), VR measured with two point probes, average VR between 1-100V

A percolation threshold of ~3,5-4,5% wt CB is indicated with the kneader, but for the twin screw extruder, not low enough amount of CB was added in order to determine the threshold.

In general, the agreement of the two methods was good. This would indicate equal mixing in both methods, but there could be major differences in microstructure. Materials with the same composition produced under different conditions may generate similar VR, but vary significantly in microstructure.

Efficient break up of CB agglomerates, that under high shear, high viscosity (low temperature) of the polymer may create a percolated network of small and well distributed small agglomerates. But an erosion process achieved by good polymer wetting and infiltration of the agglomerates, such as under low viscosity (high temperatures) of the melt may generate a percolated network consisting of well dispersed CB particles and small amounts of larger agglomerates [14].

Thus one compounding method could be breaking up agglomerates, but not wetting and distributing individual CB particles efficiently and vice versa in the other method. These hypotheses emphasize the dependence on temperature and the correlation to polymer viscosity. The materials produced with the Brabender kneader were compounded at 180 °C and the twin screw extruder was set at 205 °C. Thus, the mere temperature difference could have facilitated the variation in percolation threshold.

4.2.5 Twin screw extruder temperature profile

Different temperature settings in the twin screw extruder were also investigated. Lower temperature increases the viscosity of the melt and thus the shear. By varying the temperature in different zones of the extruder, increased shear in low temp zones and increased wetting and erosion in high temperature zones could be combined to achieve increased dispersion and distribution of CB particles and agglomerates. LLDPE and CB1 were used for these trials. Figure 15 shows the results.

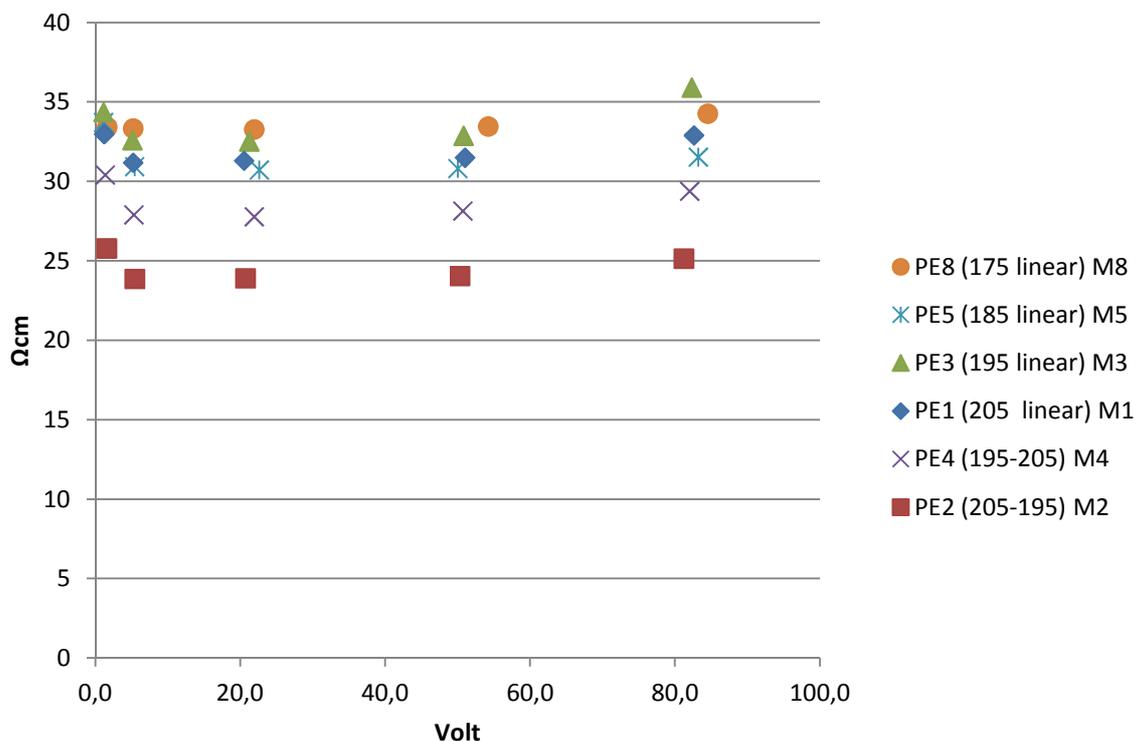


Figure 15 - LLDPE and 5% wt CB1 (materials PE1-8) compounded in a twin screw extruder with different temperature settings. The first heating zone (feed zone) was set to 165 in all trials. The heating zones 2-10, were set to a fixed temperature along the extruder called PE#(temp zone 2-10 linear), or the heating zones were divided in two segments where the heating zones 2-5 were set to one temperature and the heating zones 6-10 with a different temperature, called PE# (temp zone 2-5 – temp zone 6-10) Method name

There was no clear trend in the linear conformations. The resistivity did not depend directly on temperature, but rather an intermediate temperature of 185 has the lowest resistivity in this group.

The M2 configuration, with high temp in the first four zones and lower temp in the front (die end) of the extruder gave the lowest resistivity. It is plausible that the lower temperature increased the viscosity of the melt and generated increased shear in a favorable position on the screw e.g. where a mixing zone was located, thus facilitating better CB distribution.

Or, if the higher temperature closer to the feed zone of the extruder reduced the viscosity in the first mixing zones, wetting and eroding CB particles from the agglomerates and the decreased temperature in the front increased the viscosity and broke remaining agglomerates, thus a combined effect of eroding and breaking of agglomerates was achieved.

4.3 Fiber filled blends

The dispersion of filler in conductive polymer blends was studied by Sumita et al [16]. Interfacial tension between the polymer phases is believed to be one of the main factors determining the distribution of CB in the two phase polymer blend.

However, the transport mechanisms and rate of diffusion needs to be considered. These aspects depend mainly on the size and shape of the CB, the affinity between filler and polymer and the viscosity of the polymers. If the polymers are of similar viscosity, the surface free energy will be the main determining feature of the CB distribution. If there is a difference in surface energy between the two polymers and it is within a certain interval, then the CB will accumulate in the interface [16].

4.3.1 EBA – PA6 filled blends

In order to investigate the possibility of interfacial double percolation, a mixture of two different polymers was prepared below the melting point of one of the phases. EBA was used as a matrix material and compounded above its melting point, while fibers of PA6 were incorporated below their melting point.

Batches with different amounts of PA6 fibers were prepared, where the concentration of CB was kept at 5% wt in the EBA phase. It was assumed that no CB could enter the PA6 fibers. All CB should therefore be in the EBA phase, or in the interface between EBA-PA6.

Because CB particles contain polar groups on the surface, and the PA6 is more polar than the EBA, the carbon black should prefer to go to the interface between the PA6 fibers and the EBA matrix. The low viscosity of EBA at high temperatures should also facilitate the transport of CB within the melt. Figure 16 shows the results from conductivity measurements of EBA - CB1 - PA6 composites.

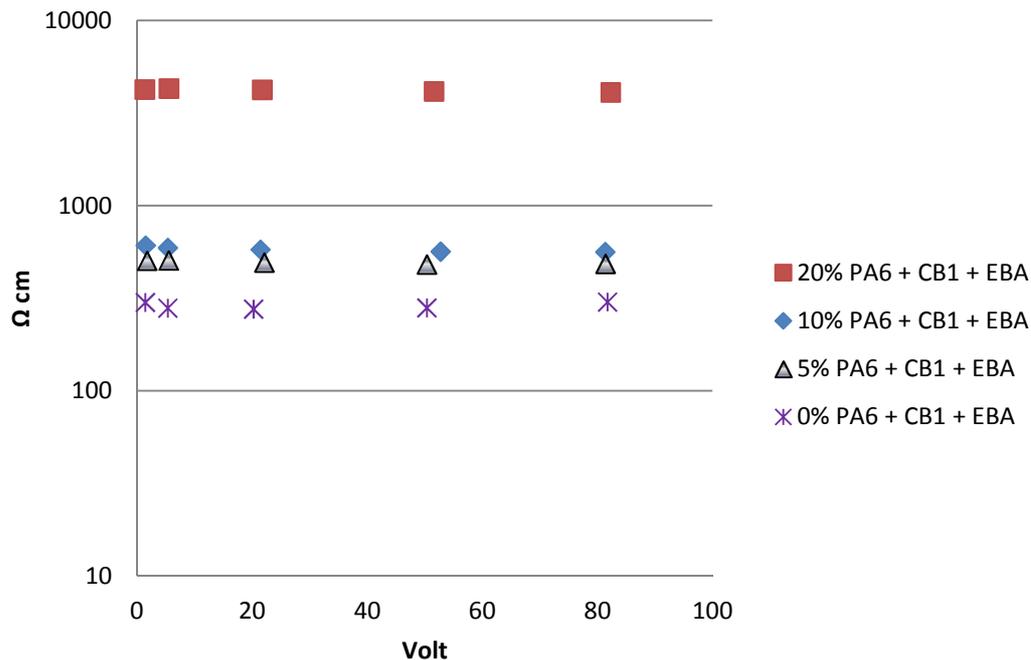


Figure 16 - EBA, PA6 and CB1 compounded at 110°C, (material EBA1-4). Various amounts of PA6 were added and the amount of CB1 was kept at 5% wt in the EBA phase

No reduction of the VR from the PA6 fiber filler was noted, but rather a slight increase with increased fiber content. Recalculating to make up for the reduced volume of EBA phase due to filler addition did not change the results significantly and will not be further discussed.

It is apparent from the VR data that no, or insignificantly little carbon black was transported from the EBA matrix to the interface. If it had, an increased amount of fiber would have lower VR than the composites with less fiber.

The combination of the very highly branched Ketjenblack CB and the slightly polar and branched EBA probably obstructs the transport of carbon black. The driving force for the CB to transport in the melt towards the PA6 surface may also be insufficient. Data on interfacial energies of this CB, PA6 and EBA have not been found and its measurement and calculation is not included in this scope, but it is one of the most important parameters of the carbon black distribution in a CPC [16]. This could be further investigated in future studies.

4.3.2 LDPE - blends

Compatibilizers

The general feature sought after in the compatibilizer in a CPC is the ability to attach dissimilar phases in the matrix to each other. This may be achieved with strong interaction, entanglement or chemical reaction. LDPE - PA6 blends have been studied with different compatibilizers.

Compatibilizer concentration

The concentration of the compatibilizer in the composite should be enough to successfully incorporate the fibers in the matrix but not so high as to disturb the matrix polymer phase and reducing its strength. Figure 17 shows the strain at break (%) of LDPE-PA6 with increasing compatibilizer concentration.

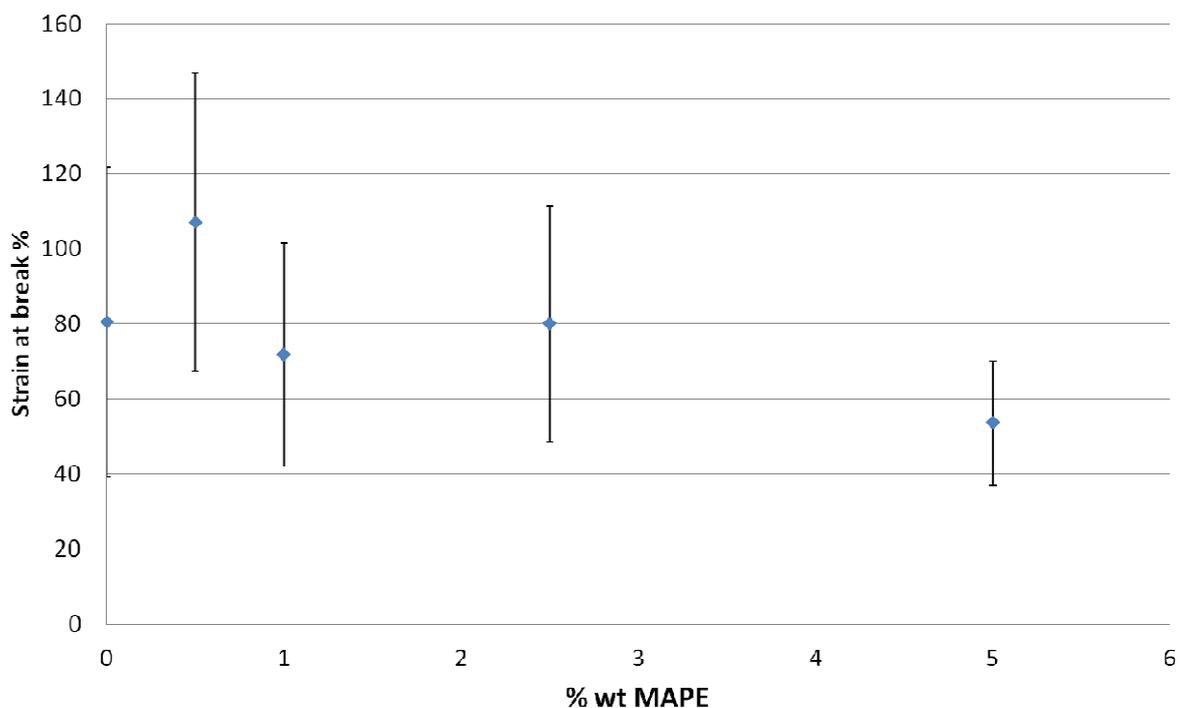


Figure 17 – LDPE with 5% wt washed PA6 fibers (materials LDPEc1-c4 and LDPEc0R1) with different amounts of MAPE.

At 0,5% wt the strain is increased, at 1% wt a slight decrease is noted, an increase at 2,5% wt and further decrease at 5% wt. There is a slight trend of decreased strain with an increased concentration of compatibilizer. However, these increases and decreases are relatively small and not statistically verified. Standard deviation is relatively high and a clear conclusion on the correct amount of compatibilizer for further investigations is not straightforward.

The MAPE, Lotader 3210 and 3410 all contain ~3% wt MA, and the AX8900 contains 8% wt GMA. The Lotader grades and MAPE are comparable in terms of reactive specie concentration. The reactivity of the GMA compared to the MA is unknown under these conditions. The GMA concentration per %wt is also higher than the MA containing samples.

Li. Z et al [17] investigated different loadings of compatibilizer. All samples contained less than 20% wt, but results showed that more than 10% wt was required to show significant macromolecular chain entanglement. However, high loadings may present other problems resulting in poor mechanical performance, and the VR may be increased. Other weaker interactions than macromolecular chain entanglement could be sufficient, allowing lower compatibilizer concentration.

Limited material amounts in combination with insufficient information on the behavior of the different compatiblizers pointed to a concentration level high enough to see the effects, but low enough not to compromise the matrix. For further investigation of compatibilizers, a concentration of 1% wt was selected.

Fiber washing

In fiber spinning and processing, different process aids are often used to ease the production. These additives may or may not influence the compatibility of the polymers. In order to remove possible process oils, simple washing with ethanol was performed. Results from mechanical testing of LDPE and PA6 fibers with and without washing is available in Table 6.

Table 6 - Influence of fiber wash on mechanical properties on LDPE-PA6 blends, 5% wt PA6 fiber

Material name	Fiber wash	Max Strain (%)	Max stress (Mpa)
LDPEc0R1	yes	81	8,5
LDPEc0R2	no	110	8,4

The effect on washing of the fibers is apparently a reduction of stress/strain. Above mentioned concentration study was conducted on washed fibers. All other testing was made on unwashed fibers.

4.3.3 Mechanical and electrical properties of compatibilized LDPE-PA6 blends

Results from mechanical testing of LDPE - CB1 - PA6 composites with MA and GMA containing compatibilizers are shown in Figure 18, and both mechanical and electrical properties are summarized in Table 7.

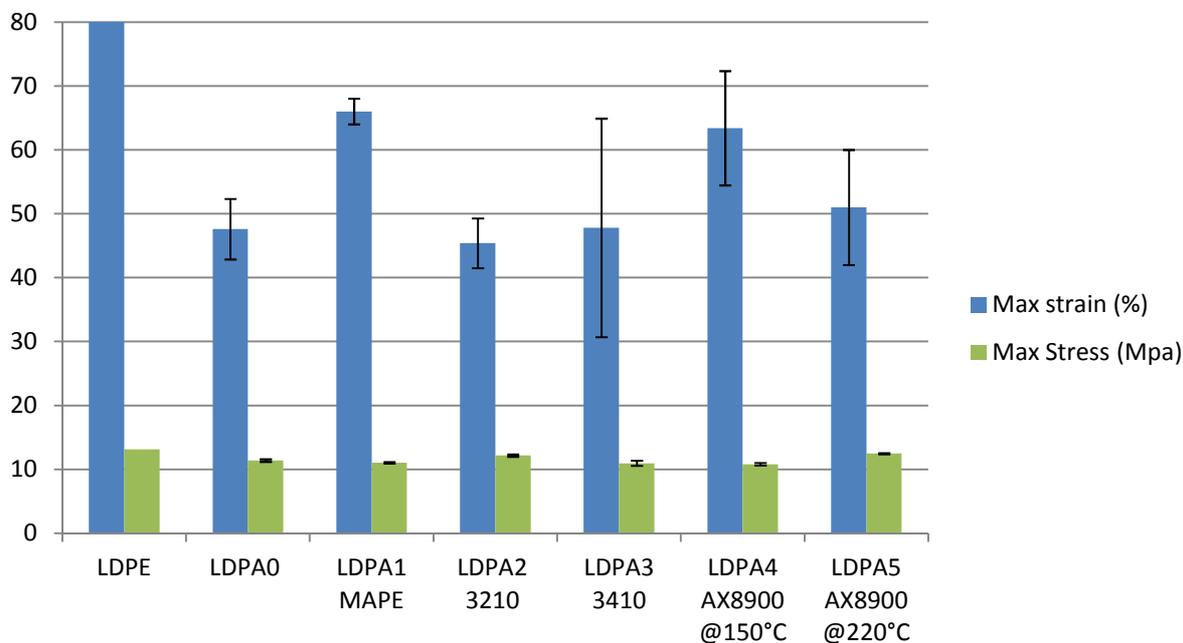


Figure 18 - Mechanical properties of LDPE and composites LDPA0-5, where MAPE 3210, 3410 and AX8900 refers to the different compatibilizers present in the sample, all compounds were produced at 150°C except for one produced at 220°C. Maximum values of stress and strain from 2 samples are presented for each compound. Virgin LDPE has a max strain of 490%

Table 7 - Mechanical and resistivity data of LDPE - fiber blends with and without different compatibilizers, average values from three samples, resistivity values measured with four point probes, (VR for LDPE was not measured but is significantly higher than any of the composites)

Material	Comp.	CB (%wt)	Fiber (%wt)	Max strain (%)	Max Stress (Mpa)	Res. (Ω cm)
LDPE	-	-	-	490	13	-
LD 1	-	10% CB1	-	11	13	7,2
LDPA 0	-	5% CB1	5% PA6	48	11	93
LDPA 1	MAPE	5% CB1	5% PA6	66	11	140
LDPA 2	3210	5% CB1	5% PA6	45	12	49
LDPA 3	3410	5% CB1	5% PA6	48	11	85
LDPA 4	AX8900	5% CB1	5% PA6	63	11	91
LDPA 5 (@220°C)	AX8900	5% CB1	5% PA6	51	12	45
LDRF 1	MAPE	5% CB1	5% Resistat	27	12	56
LDRF 2	MAPE	5% CB1	7,8% Resistat	21	11	51

General trends

The max stress was not significantly affected by any of the additives. None of the composites have a max strain in line with the virgin LDPE.

In general, the addition of fibers and CB reduced the max strain and resistivity compared to virgin LDPE. The volume resistivity of all compatibilized blends are on the same level, thus the overall effect on VR from the compatibilizers is small. Small differences in max strain of the fiber containing blends may be observed. The strain depended on the compatibilizer type, fiber content and fiber type.

The lowest value of resistivity was obtained with LD1, but the CB content was a significantly higher than in any of the fiber containing blends and the max stress was the lowest of them all.

MAPE –(MA) - LDPA 1

The highest max strain was obtained with LDPA1. It was significantly higher than the strain of LDPA0 (without compatibilizer). This indicates compatibilization of PA6 in LDPE with MAPE.

However, LDPA1 also had a slightly higher resistivity than the other compatibilized blends. The aliphatic graft on the MAPE could have better solubility in LDPE than the grafts of the other compatibilizers, thus migrating more towards the matrix during the compounding. The MAPE may there have encapsulated CB, hindering erosion of CB particles from agglomerates or it may have built up a shielding layer on the CB agglomerates, protecting them from rupture, resulting in slightly higher VR.

Lotader AX8900 – (GMA) - LDPA 4&5

Promising results on mechanical properties of HDPE - PA11 composites with PE-g-GMA have been described in literature. Grafting reactions between PA and PE-g-GMA were confirmed, and an optimum compounding temperature of 230 °C was reported [2].

In this work an *LDPE-PA6* composite with EMA-g-GMA was studied, and it was compounded at lower temperatures. The LDPA4 with had a similar max strain as LDPA1, and both have higher max strain than LDPA0. These results may be viewed as a minor success in compatibilization.

An increased temperature would possibly increase the reaction speed of the GMA-PA6 grafting and improve the mechanical properties, however, max strain was reduced when compounding at higher temperature, LDPA5. When the temperature was increased, the fibers may have fragmented in smaller parts or droplets. With poor compatibilization and an increased number of particles, the composite may have become more fragile. More possible points of break initiation would result in lower elongation before break.

It is possible that both compounding temperatures were too low for sufficient grafting reaction to take place between the GMA and the PA6. The fact that the PA6 is compounded below its melting temperature may also significantly decrease the reactivity between PA6 amide groups and GMA. But studies by Abraham T.N et al [18, 19] indicate good mechanical performance without melting of the PA6. High mechanical performance and good recycling properties of HDPE - PA6 composites with MA compatibilizers is reported. The reprocessing of the HDPE - PA6 blends was performed above and below the melting point of nylon and both generated improved mechanical properties as compared to virgin HDPE [18, 19].

But the compatibilizer used in the study by Abraham T.N et al was an MA compatibilizer, which is different from the GMA compounded at high temp in this study. Conclusions on the grafting reaction may not be drawn from these data. In order to determine actual grafting reaction between the PA6 and GMA in this study, further investigation is needed.

The compatibilizer graft used in the above mentioned study could have been more suitable for their matrix polymer than achieved in this study. The polymer grafted with the GMA in AX8900 (EMA) contains high amounts of methyl acrylate (24% wt), and is thus very polar. It may thus have had unfavorable or insufficient interactions with the LDPE matrix.

The VR of LDPA4 is very close to LDPA0, indicating that the influence on the CB dispersion was low. Migration towards the matrix is less likely compared to MAPE, when considering the high polarity of the PE graft in AX8900. Since the matrix is non polar LDPE, the driving force towards migration towards the matrix is low.

The resistivity was reduced when using an elevated temperature, LDPA5. The elevated temperature was not above the melting temperature for PA6 and thus CB would still not enter the PA6 phases, keeping the volume exclusion effect. The further reduction in resistivity may be due to decreased viscosity in the melt, facilitating increased CB dispersion during mixing.

Lotader 3210&3410 – MA - LDPA 2&3

The materials produced with Lotader grades 3210 and 3410 (LDPA2&3) have the lowest elongation. Both contain EBA copolymer grafts and the polar comonomer (butyl acrylate) content of 3210 is 6% wt and of 3410 is 17% wt.

Both compatibilizers contain the same amount of MA. Reactive compatibilizers based on MA were studied by Li. Z et al [17] who claim that the compatibilizer efficiently enhanced the compatibility between HDPE and PA6. Jiang et al [11] concluded that the solubility of the compatibilizer in PE should not be too great. The PE in the PE-g-MA Lotader grades contains polar copolymers which could be sufficiently in-soluble in LDPE matrix.

The compatibilizer with a higher BA content generates a material with slightly higher max strain. But both more polar AX8900 and less polar MAPE both produce composites with higher max strain. MAPE contains the same reactive specie (MA) as 3210 and 3410, but is

aliphatic and AX8900 contains GMA but is more polar, or in the same polarity region as 3410. Thus it is not just the polarity of the graft that reduces the max strain.

Literature indicates MA to be reactive towards PA6 and materials produced with MAPE have higher strain than the reference, and thus MA is probably suitable for the compatibilization of PA6. Uncertainties in the efficiency of GMA-PA6 grafting reaction at the chosen compounding temperatures prevent thorough conclusions in the comparison of GMA vs. MA.

The grafted BA may have insufficient or unfavorable interactions with the LDPE matrix. In combination with SEM pictures taken and further testing of e.g. impact strength, a better picture of the mechanical performance of these blends may be achieved.

The VR of both LDPA2&3 were lower than LDPA1&4, and that of LDPA2 was one of the lowest. This could indicate that the interaction with the matrix was weak, thus not migrating in the matrix and influencing the CB distribution. If the least interaction with the matrix was obtained with these compatibilizers, the reactivity of the MA comes into question. It is possible that moisture in the sample bags or in the PA6 during compounding or contaminants have consumed the MA and thus not leaving enough to react with the PA6. If it was during compounding, the MAPE grade should also be affected.

Resistat fibers

A PA6,6 fiber with CB suffused in the surface, Resistat fiber, was also investigated. Two compounds containing these conductive fibers were produced and MAPE was used in both formulations. The resistat fibers reduced the VR compared to LDPA1, but no extreme effect is noted. The VR reduction may be a slight effect from the carbon suffused in the surface of the resistat fibers, but more probably, it is an effect of the difference in fiber geometry and size distribution.

VR decreased with higher fiber content, but this may also be a volume exclusion effect since LDRF1&2 were compounded below the melting temperature of the fibers. The max strain was also reduced, indicating poor compatibilization of the fibers, or another effect from the geometry. If better control of fiber size and size distribution could be achieved, further investigations could generate interesting results. Higher fiber content with a suitable compatibilizer may produce materials with good mechanical properties and super low percolation threshold.

Many of the articles have discussed the compatibilization of HDPE [17, 18, 19], whereas this study focuses on LDPE. The difference between HDPE and LDPE should not influence the reactivity of the MA or GMA towards the PA6, but rather the matrix interactions.

Optical microscopy

The reinforcing property of the fiber geometry was diminished by the fact that the PA6 fibers curled up during compounding, thus not providing strength to the composite, but rather acted

like a soft spring or gave no effect at all. This is evident from the optical micrograph of one of the LDPE-PA6 composites in Figure 19.

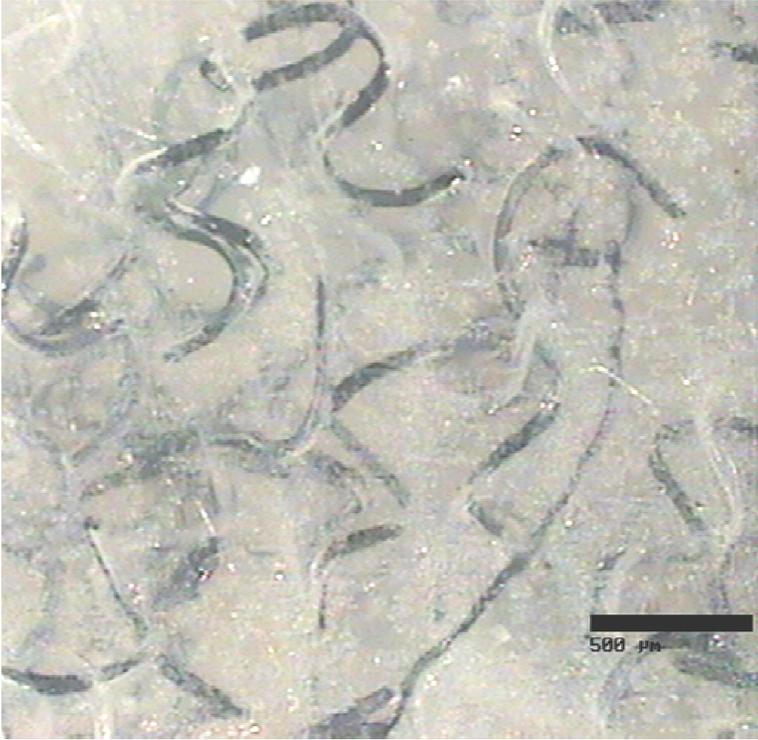


Figure 19 - Optical micrograph of PEC4, compression moulded plaque, showing curled PA6-fibres embedded in the matrix.

All fibers have curled up and voids appear to be present in the material. It is possible that with the bad compatibilization of the fiber, voids are created during stress. The voids could also be the result of water vapor escaping from the fibers, if the PA6 was not completely dried out. A material similar to foam is thus formed, with fibers inside the voids. This is illustrated schematically in Figure 20.

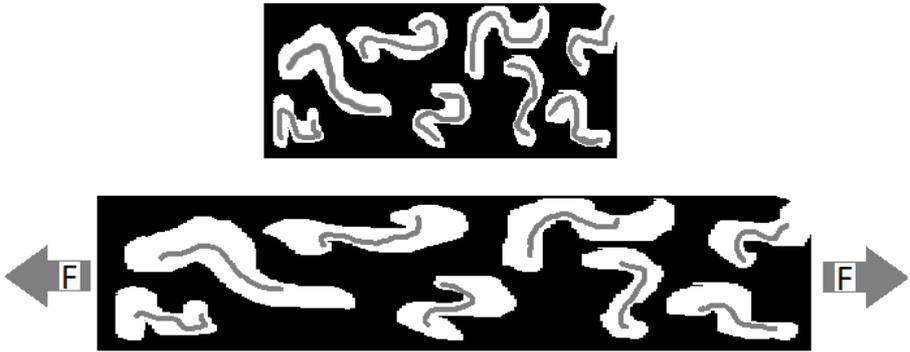


Figure 20 – Cross section of a fiber composite with poor compatibilization, black fields representing the matrix polymer, grey areas represent the fibers and white areas are voids, without stretching (above) and without stretching (below)

SEM imaging

In order to further investigate the effect of the compatibilizers, SEM images of two LDPE-PA6 composites with two different compatibilizers were obtained. A SEM image of PEc4 is shown in Figure 21. A close-up of the left right corner is observable in Figure 22.

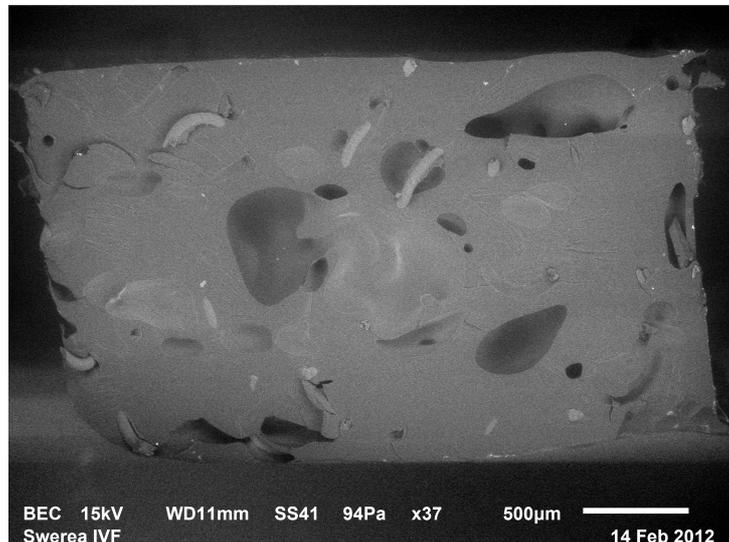


Figure 21 - SEM image of a cryofractured surface of LDPEc4 (with MAPE) from a plaque compression moulded with slow cooling, image obtained at 15kV, 94Pa, x37 magnification

Large voids without fibers present are apparent in the SEM image. These are believed to originate from water present in the material from insufficient drying of the materials, or air pockets created during compression moulding. However, the MAPE used in this sample may have been acting well as a compatibilizer when viewing the close-up in Figure 22.

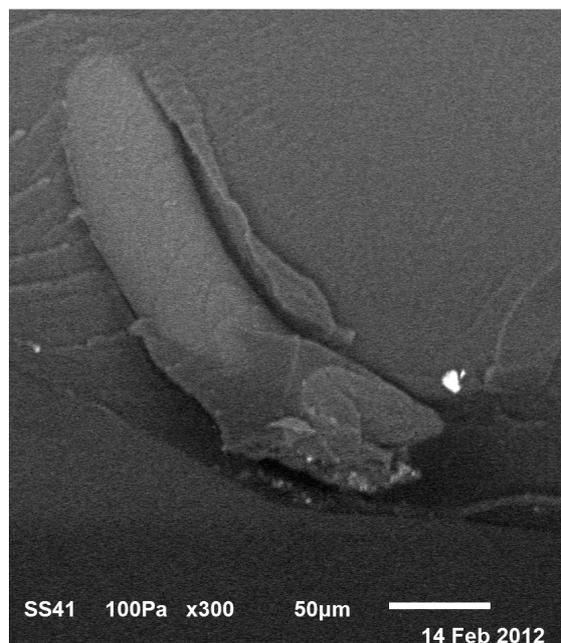


Figure 22 – Close up of the bottom left corner of Figure 21, SEM image of a cryofractured surface of LDPEc4 (with MAPE) from a plaque compression moulded with slow cooling, showing one of the PA6 fibers protruding from the cryofractured surface, image obtained at 15kV, 100Pa, x300 magnification

There was no void in the area where the fiber emerges from the matrix. The void between the protruding part of the fiber and the matrix could have been created by the cryofracturing. There were also some residues on the protruding fiber that could be remnants of compatibilizer or matrix stuck to the fiber. This is not evident in the LDPEc34 sample shown in Figure 23.

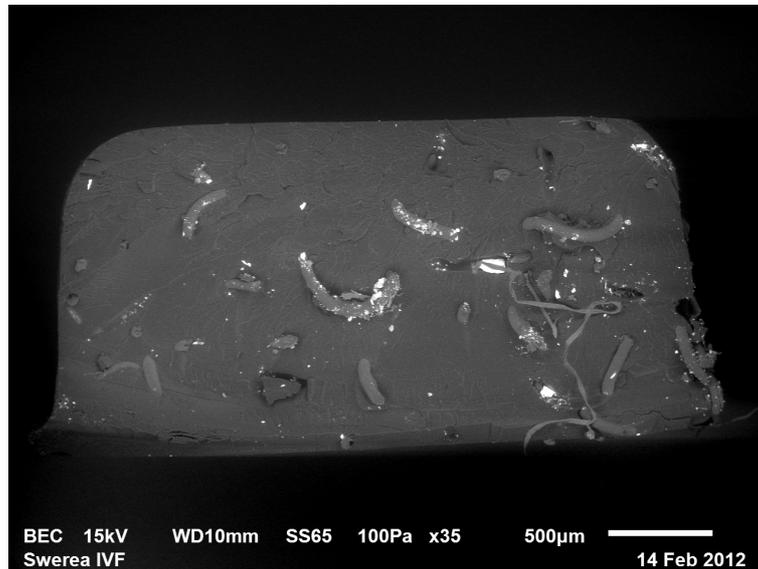


Figure 23 - SEM image of a cryofractured surface of LDPEc34 (with Lotader 3410) from a plaque compression moulded with slow cooling, image obtained at 15kV, 100Pa, x35 magnification

No large voids are present in this sample, but several bright spots indicate impurities. These impurities are concentrated at the fiber surfaces. A close-up of the upper left corner is shown in Figure 24.

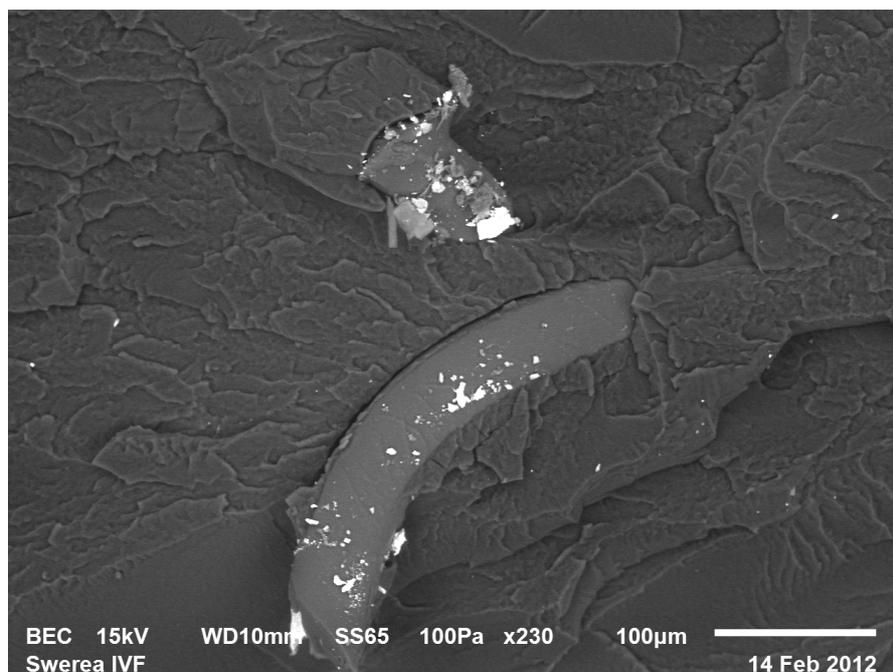


Figure 24 - Close up of the bottom left corner of Figure 21, SEM image of a cryofractured surface of LDPEc34 (with Lotader 3410) from a plaque compression moulded with slow cooling, showing two of the PA6 fibers protruding from the cryofractured surface, image obtained at 15kV, 100Pa, x230 magnification

Voids between the fiber and the matrix are apparent. The fibers have delaminated from the matrix and no clear signs of residues other than the contaminants could be observed on the fiber surface.

An EDX investigation of the bright spots showed high levels of iron and aluminum oxides, which could have originated from contaminants in the compounding unit. But since the contaminants are not present in the LDPEc4 sample which was produced with ethanol washed fibers, the contaminants could have been on the fibers from the manufacturer, or ended up on the fibers during handling. If that was the case, more contaminants distributed in the rest of the composite would have been expected.

However, the oxides are polar and the matrix is not. Thus the interfacial energy between them and the matrix may be higher than that of the oxides and the PA6 fibers. The matrix may also have rejected the contaminants, forcing them towards any void in the material. Thus a driving force towards the PA6 surface or delamination voids may have been created and consequently the oxides accumulated there.

LDPEc34 and LDPEc4 were not compounded at the same date, and others have used the equipment in-between. Thus contaminants that were not there before could have been introduced in the kneading mixer, and the fiber washing could have had nothing to do with this. New compounds were produced after thorough cleaning of the compounding unit, but SEM imaging has not been performed. This could be interesting in future studies.

The compatibilizing effect from the Lotader 3410 may have been incapacitated by side reactions with oxides instead of PA6. This would severely reduce the max strain of the material, but also the oxides themselves may act as break initiators. Further studies to investigate the extent of contaminants in the other samples would provide valuable information on the cause of mechanical behavior.

The compound compatibilized with Lotader 3410 also had low strain at break compared to the MAPE containing material. If the differences are due to voids, contaminants or differences in compatibilizer efficiency is not completely understood, but indications of achieved compatibilization are evident from SEM image and mechanical data of PEc4. Reduced mechanical properties and lots of contaminants are shown in PEc3410.

4.4 PEX filled blends

Several composites with cable production scrap and end of use cable scrap from the high voltage cable industry were produced and evaluated with respect to their mechanical and electrical performance. LDPE and HDPE were used as matrix polymers and CB1 and CB2 were used as conductive fillers.

4.4.1 DSC of PEX filled blends

Figure 25 shows the DSC investigation of the recycled PEX materials. Evidence of un-reacted peroxide could be observed.

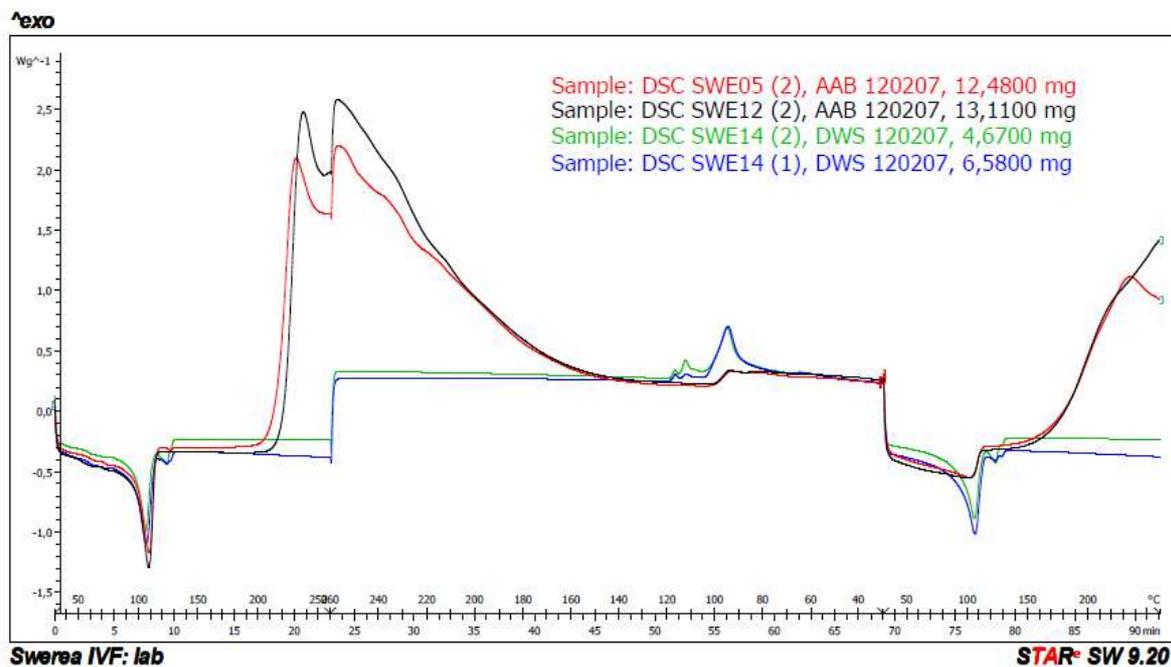


Figure 25 - DSC of PEX materials, (SWE05 red, SWE12 black, SWE14 green and blue), heating rate 10°/min cooling rate 5°/min

All samples show an endotherm at ~100 °C, around 5-8 min. This is associated with melting of the crystalline phases of the polymer. The exotherm at ~23 min occurs in all samples and is believed to be related to instabilities in the equipment during switch over from heating to cooling possibly in combination with degradation of the sample.

In samples SWE 12 and SWE5, a high exotherm at ~18 minutes is believed to be related to a cross linking reaction due to un-reacted peroxide present in the sample. This exotherm is not present in the SWE14 sample.

The crystallinity of SWE5 and 14 is also observed to decrease from the first heating stage (0 - 23 min) to the second heating stage (69 - 90 min), further adding to the cross linking theory. At 50-60 minutes, the SWE14 show an endotherm, related to formation of crystals, which is absent in the SWE5 and 12 indicating a reaction has taken place in these samples, reducing the formation of crystals. The endotherm related to melting at ~75 minutes is much smaller in

SWE5 and 12 compared to SWE14, since fewer crystals to melt have been formed in these samples.

The exotherm present in SWE5 and 12 in the last 10 minutes is related to further degradation of the sample.

4.4.2 Extraction of PEX and PEX filled blends

Extraction in decalin in order to determine gel content was conducted. The sample SWE12XL was pretreated in an oven at 180 °C for 60 minutes in order to allow the residual peroxide to react. However this did not change the cross linking degree, compared to the untreated batch of the same sample, SWE12.

From the DSC measurements it may be concluded that the cross linking reaction occurred very slowly or not at all, at temperatures lower than 200 °C. Table 8. shows the results from the extractions.

Table 8 - Not extractable fractions from extraction of PEX compounds

	SWE 12XL	SWE 12	SWE 5	SWE 14	S5	LDPX 1	PS1
%wt Not extracted	79%	79%	76%	56%	5%	44%	0%
STD dev	0,001	0,001	0,0004	0,01	0,002	0,001	0,05

S5 was obtained from pulverized cable production waste lumps. This sample showed very little insoluble material and is not considered to be cross linked. Trials with compression moulding showed that the material cross links if sufficiently heated, thus the sample did contain peroxide.

The sample PS1 contained 20% wt of S5, and a small negative result was interpreted as 0% wt insolubles combined with an error in measurement. None of the peroxide was thus reacted during compounding at that compounding temperature.

SWE 14 contained 56% wt extractables, but is considered fully cross linked when the DSC results are taken into consideration. No evidence of un-reacted peroxide could be found. There were some thermoplastic fractions in this batch, confirmed by compression moulding trials.

SWE 12 was considered fully cross linked, but the DSC results (see Figure 25) show evidence of residual peroxide. Peroxide may have been present in excess. It is possible that cross linking of the matrix may have taken place during compounding and sample preparation of LDPX1, due to the presence of the residual peroxide.

The LDPX1 contained 50% wt of SWE12 and the non extractable part of SWE 12 is 79% wt, thus the theoretical amount of non extractables in LDPX1 is 40% wt. The fact that 44% wt of the material is not extractable is possible to interpret as additional cross linking to have taken place from residual peroxide in SWE12.

This may also be a result of CB migrating into the softened XLPE grains during compounding. The CB may subsequently have stuck there hard enough not to be extracted. The weight of the extracted sample is thus increased by CB embedded in the PEX particles, appearing to increase the degree of cross linking.

4.4.3 Conductivity of PEX filled blends

When a non melting phase such as the XLPE is introduced in the composite, the carbon black is forced to stay in the thermoplastic matrix during compounding. This may be interpreted as a volume reduction of the continuous LDPE-CB phase. This is illustrated schematically in Figure 26.

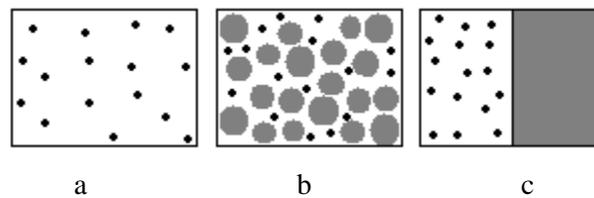


Figure 26 - CB distribution of a CPC with an impenetrable filler represented by the gray fields, CB is represented by black dots and the matrix polymer is white, to the left (a) is the matrix polymer with X% CB, in the middle (b) matrix polymer with X% CB and 50% filler, to the right (c) is an equivalent distribution of CB assuming no interaction between the filler and the CB

Figure 26 (a) shows a sample of a matrix polymer at some fixed concentration of CB. If impenetrable filler such as PEX is introduced and the concentration of CB is kept fixed (b), the matrix will have a higher CB content, and the volume is reduced (c). Recalculating the results from the samples containing SWE12 using Eq. 3 would provide results which are more comparable between materials with and without filler.

$$\rho(V2) = \rho(V1) * wf \quad \text{Eq. 3 - VR adjusted for volume exclusion effects}$$

Where $\rho(V2)$ is the recalculated volume resistivity (Ωcm), $\rho(V1)$ is the measured sample volume resistivity (Ωcm) and wf is the weight fraction of impregnable filler in the composite (%wt).

4.4.4 LDPE – PEX blends

LDPE compounds produced with different amounts and types of CB and XLPE were compounded. The results from electrical and mechanical testing are shown in Table 9.

Table 9- Mechanical and VR data of LDPE composites including VR data where reduced volume has been taken into account (Comp. Resist.)

Material name	CB (%wt)	Filler (%wt)	Max strain (%)	Max stress (MPa)	Resist. (Ω cm)	Comp. Resist. (Ω cm)
LDPE	-	-	491	13	-	-
LD 1	10% CB1	-	11	13	7	-
LDPX 1	5% CB1	50% SWE12	314	14	24	12
LDPX 2	5% CB1	25% SWE12	347	14	44	33
LDPX 3	7% CB1	25% SWE12	-	-	16	12
PS 1	5% CB1	25% S5	300	14	2400	-

When comparing the mechanical properties in Table 9, little or no effect on the max stress was seen with any of the additives. All composites showed a reduced max strain compared to virgin LDPE. A strong reduction in max strain is observed in LD 1, which was also noted during sample preparation where this compound was very brittle. All SWE12 containing composites have similar max strain.

The LDPX1 should have similar VR results compared to LD 1, since the SWE12 addition may be viewed as a volume reduction of the matrix by 50%, if the polymers are assumed to have similar density. Thus 5% wt total CB content in LDPX1 was 10% wt CB in the matrix. The VR values were as assumed, very similar and the slight deviation could be because of the SWE12 was not fully cross linked and some CB may have penetrated the SWE12 phases of LDPX1, thus increasing the VR slightly.

The difference between the samples with 25% wt and 50% wt XLPE is comparatively small. Thus the loading of PEX may be increased without significantly lowering the max strain and simultaneously reduce VR. The LDPX3 has an equal VR LDPX1, but no data has been obtained on mechanical properties. This indicates that the amount of PEX may be high in combination with low CB content without increasing VR.

It was evident that the sample containing the S5, which was not cross linked, had a significantly higher volume resistivity than all the other samples. This suggested that the carbon black had entered the thermoplastic phases of S5 and thus the composite was diluted and fewer conductive pathways were created. The max strain was the lowest in the group with PEX additives, which may indicate poor compatibility between the LDPE and the thermoplastic polymer mix of S5.

4.4.5 HDPE-PEX blends

HDPE compounds produced with and different amounts and types of CB and XLPE from recycled cable batches were compounded. The results from electrical and mechanical testing are shown in Table 10.

Table 10 - Mechanical properties and VR of HDPE composites with two different types of CB, with and without PEX, average of 3 samples, Comp. Resist. refers to VR values where calculations using eq.3 have been made to compensate for volume exclusion effects from the PEX

Material name	CB (%wt)	Filler (%wt)	Max strain (%)	Max stress (MPa)	Resist. (Ω cm)	Comp. Resist. (Ω cm)
HDPE	-	-	7,7	31	-	-
HD 1	10% CB1	-	1,1	25	3,9	-
HDPX 1	5% CB1	50% SWE12	37	19	39	20
HDPX 2	5% CB2	50% SWE12	22	19	3720	1859
HDPX 3	10% CB2	50% SWE12	6,8	17	562	281

Compared to the virgin HDPE, all samples show a reduced max stress. An increased max strain is seen in all samples with an addition of SWE12. The VR is very low for the HD 1, but the max strain is the lowest. The high concentration of CB1 made the material very brittle, the sample crumbled easily which also made sample preparation difficult. With the addition of SWE12 and 5% wt CB1, the max strain increased significantly compared to both virgin HDPE and HD 1.

The VR of HDPX 1 increased by only 80%, when comparing to the HD 1. This would indicate that with the addition of recycled PEX, a much more ductile material with the same level of VR could be achieved with a reduced amount of CB.

The composites containing CB2 have similar max stress as the ones with CB1, but the max strain is less and the VR is significantly increased. The HDPX 2 has higher VR but also higher max stress and strain compared to HDPX 3.

The size and shape of the CB agglomerates is crucial to the conductivity. The CB2 is not as branched as CB1, and the agglomerates are bigger. Thus the concentration of CB2 needs to be significantly higher to obtain the same level of resistance. The concentration of CB2 was not high enough to reduce the VR significantly and too high to generate high stress and strain. Thus increasing the CB2 content is not advantageous.

The compounding technique could perhaps be optimized. Data from the producer of CB2 indicate that increased mixing time increases the volume resistivity of the produced material. This is especially pronounced at mixing times over 7 minutes [20]. In this study, 12 minutes mixing time was used, which may not be suitable for this CB. Alternatively, a different CB with higher resistance to over mixing could be chosen for further investigation.

5. Conclusions

This study has shown that it is possible to increase the conductivity and improve mechanical properties of CB-PE blends by adding PEX particles.

PEX fillers improve the mechanical properties and the electrical conductivity of both HDPE and LDPE blends. More ductile materials are achieved with PEX-HDPE-CB composites, than HDPE-CB composites. The degree of cross linking of the recycled material is important for both mechanical properties and electrical conductivity. When adding cross linked recycled PEX to the composite, less virgin polymer and less CB needs to be added to achieve the same electrical conductivity and keep or increase max stress and strain. Cost reduction is thus possible by using recycled PEX materials. Thus cheaper, more ductile materials with low resistivity may be produced from recycled cable waste.

The mixing of polyamide fibers with PE-CB blends did not improve any properties significantly. The addition of compatibilizers did not achieve significant improvements. The lowest VR was achieved when using Lotader 3210 or compounding at higher temperature with AX8900.

The Resistat fibers did not significantly reduce the VR. Limited control over fiber size and size distribution made comparison difficult. Increased fiber content should be studied.

6. Future work

This study has shown that the compatibilization of PA6 in LDPE is not straightforward. The concentration and type of compatibilizer has not been fully optimized and further testing on this subject could be interesting. However, since the fibers are not intact during compounding (they curl up), another PA6 or PA6,6 geometry may be more advantageous.

Testing of the compatibilizers in an EBA-PA6 composite has not been tested in this study, but may provide valuable insights and generate interesting materials.

Further studies with SEM-EDX should be performed in order to investigate the extent and cause of contaminants and determine the validity of the mechanical data. New compounds were produced for conductivity measurements, but no SEM-EDX study was made on these.

In order to choose the optimal matrix-CB-filler compound the driving force of the CB for migration towards the filler surface could be studied. The interfacial energy of the constituents is one of the most important parameters of the carbon black distribution in a CPC. Determining these data for the system would provide a valuable decision basis in selecting promising composite constituents.

Charpy/Impact testing could provide further insight in the mechanical properties of the composites and give further indications of what the materials may be used for.

The compounding time may have been too long, damaging the CB structure and possibly encapsulating CB particles in non conductive matrix. Optimizing compounding time and temperature for each composite would generate better data for comparison. Also, a different CB with similar price and structure to CB2 but better resistance to over mixing could be used instead of CB2 to compare the composites.

Testing an increased number of specimens and a statistical analysis could be conducted in order to statistically verify all results.

Further extraction experiments and DSC investigations could be performed to confirm cross linking of samples containing residual peroxide and grafting reactions in the compatibilizer study.

7. Acknowledgements

I would like to express my gratitude to my supervisor Martin Strååt, who supported me throughout the whole project; this work would not have been possible without his guidance, encouragement and support

I sincerely wish to thank Swerea IVF and staff for an instructive and inspiring experience, and in particular Thomas Sjöholm and Erik Nilsson, whose support and exchange of ideas were invaluable.

I gratefully acknowledge Christer Svanberg for his innovative ideas and great expertise.

I owe my deepest gratitude to Borealis AB in Stenungsund for supplying materials and for letting me use equipment at the Innovation Center. Thanks to all lab personnel involved and special thanks to Kjell Fossum and Ann Karlsson for the booking, planning and operation of equipment and Ingela Wastegård for material distribution.

I am deeply grateful to Professor Mats Andersson for his supervision and support.

My heartiest thanks to Rikard in supporting me and for proofreading my thesis.

8. Appendices

Appendix I – Compounding settings and materials produced

References

- [1] M. Lewin, E.M Pearce (1995) *Fiber Chemistry – Handbook of fiber science and technology* Vol. 4, Marcel Dekker INC
- [2] E. G. Koulouri, A. X. Georgaki, J. K. Kallitsis (1997) *Reactive compatibilization of aliphatic polyamides with functionalized polyethylenes* Polymer Vol. 38 No. 16
- [3] S. H. Foulger (1999) *Reduced percolation thresholds of immiscible conductive blends* Journal of polymer science Part B Polymer Physics, Vol. 37, p. 1899-1910
- [4] A. Brent Strong (2006) *Plastics – Materials and processing*, 3rd ed. New Jersey: Pearson Education Inc
- [5] M. Weber, M. R. Kamal (1997) *Estimation of the Volume resistivity of electrically conductive composites* Polymer composites Vol. 18, No. 6, p. 711-725
- [6] H. Kesten (2006) *What is percolation* Notices of the AMS Vol.53 No. 5 p. 572-573
- [7] G. Grimmett (1999) *Percolation* 2nd ed. Berlin: Springer
- [8] M. Xanthos (2010) *Functional fillers for plastics* 2nd ed. Wiley-VCH
- [9] F. Gubbles, R. Jerome E. Vanlathem, R. Deltour, S. Blacher, F Brouers (1998) *Kinetic and thermodynamic control of the selective localization of carbon black at the interface of immiscible polymer blends* Chem mater, Vol. 10 p. 1227-1235
- [10] J.L. White, E.K. Kim (2010) *Twin screw extrusion – Technology and principles* 2nd Ed. Hanser Publications
- [11] C. Jiang, S. Filippi, P. Magagnini (2003) *Reactive compatibilizer precursors for LDPE/PA6 blends - II: maleic anhydride grafted polyethylenes* Polymer Vol. 44 p. 2411–2422
- [12] Arkema, Lotryl webpage *Lotryl® - Product Info* Online (2012-04-16)
URL:http://www.arkema.com/sites/group/en/products/detailed_sheets/technical_polymers/lotryl/product_info/home.page
- [13] Arkema, Lotader webpage *Lotader® - Product Info* Online (2012-04-16)
URL:http://www.lotader.com/sites/group/en/products/detailed_sheets/technical_polymers/lotader/product_info/home.page

- [14] G. Kasaliwal, A. Gödel, P. Pötschke (2009) *Influence of Processing Conditions in Small-Scale Melt Mixing and Compression Molding on the Resistivity and Morphology of Polycarbonate–MWNT Composites* Journal of Applied Polymer Science, Vol. 112, p. 3494–3509
- [15] F. Gubbels, S. Blacher E. Vanlathem, R. Jerome, J R. Deltour, O.F. Brouers, Ph. Teyssie (1996) *Design of Electrical Conductive Composites: Key Role of the Morphology on the Electrical Properties of Carbon Black Filled Polymer Blends* Macromolecules Vol. 28, p. 1559-1566
- [16] M. Sumita, K. Sakata, S. Asai, K. Miyasaka, H. Nakagawa (1991) *Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black* Polymer Bulletin Vol. 25 p. 265-271
- [17] Z. Li, Y. Hongmei, S. Yonggang, Z. Farao, Z. Qiang (2008) *Morphological evolution and viscoelastic behavior of compatibilized HDPE/PA6 blends* Acta polymerica Sinica Vol. 9 p. 849-856
- [18] T.N. Abraham, K.E. George *Recyclable nylon reinforced HDPE composites: Effect of fiber diameter* Progress in rubber, plastics and recycling technology Vol. 23 No. 3 p. 153-167
- [19] T. N. Abraham and K. E. George (2005) *Studies on recyclable composites: nylon fibre reinforced high density polyethylene composites* Plastics Rubbers and Composites Vol. 34 No. 4 p. 196-200
- [20] Timcal graphite and carbon, *Carbon Additives for Polymer Compounds*, Online (2012-04-18) URL: [http://www.timcal.com/scopi/group/timcal/timcal.nsf/pagesref/MCOA-7S6HTN/\\$File/TIMCAL_brochure_carbon_additives_for_polymer.pdf](http://www.timcal.com/scopi/group/timcal/timcal.nsf/pagesref/MCOA-7S6HTN/$File/TIMCAL_brochure_carbon_additives_for_polymer.pdf)

Appendix I – Compounding settings and materials produced

Table 1- Mixing temperature and conditions in the Brabender kneading mixer

Method name	Temp (°C)	rpm	Total mixing time (min)	Comment
Mix 1	110	50	12	2 min melting of EBA, add CB, mix 5 minutes, additional additives, mix 5min
Mix 2	90	65	12	2 min melting of EBA at 90°C, add CB, mix for 10 min
Mix 3	170	50	12	2 min melting of LLDPE, add CB, mix 5 minutes, additional additives, mix 5min
Mix 4	140	70	12	2 min melting of LLDPE, add CB, mix 5 minutes, additional additives, mix 5min
Mix 5	150	50	12	2 min melting of LDPE, add fiber/compatibilizer dry blend, mix 10 min
Mix 6	150	50	10	5 min melting LDPE/compatibilizer dry blend, then add fiber and mix for 5 min
Mix 7	180	50	10	5 min melting LDPE/compatibilizer dry blend, then add fiber and mix for 5 min
Mix 8	150	50	12	Dry blend all components, mix for 12 min
Mix 9	180	50	12	Dry blend all components, mix for 12 min
Mix 10	220	50	12	Dry blend all components, mix for 12 min
Mix 11	190	50	12	Dry blend all components, mix for 12 min
Mix 12	260	100	10	2 min melting of PBT, add CB, mix 8 minutes

Table 2- Mixing temperature (starting with the feed zone) and settings in the twin screw extruder

Method name	Temp (°C)	Screw rate rpm	Feed rate Kg/h
M1	160 / 195 / 205 / 205 / 205 / 205 / 205 / 205 / 205 / 205	200	10
M2	160 / 195 / 205 / 205 / 205 / 205 / 195 / 195 / 195 / 205	200	10
M3	160 / 195 / 195 / 195 / 195 / 195 / 195 / 195 / 195 / 195	200	10
M4	160 / 195 / 195 / 195 / 195 / 195 / 205 / 205 / 205 / 205	200	10
M5	160 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185	200	10
M6	160 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185	200	7,5
M7	160 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185 / 185	200	15
M8	160 / 175 / 175 / 175 / 175 / 175 / 175 / 175 / 175 / 175	200	10

Table 3 - Material composition, where *PA6F* contains polyamide 6 fibers and *PA6WF* contains ethanol washed PA6 fibers, *ReF* is conductive polyamide 6,6 fibers called resistat, *comp* refers to compatibilizer, *3210* contains Lotader 3210, *3410* contains Lotader 3410 and *AX89* contains Lotader AX8900.

Material Name	Mix Method	% wt Matrix Material	% wt Cond. filler	% wt Filler	% wt Comp.
EBA 1	Mix1	95% EBA	5% CB1	-	-
EBA 2	Mix1	76,2% EBA	3,8% CB1	20 % PA6F	-
EBA 3	Mix1	85,7% EBA	4,3% CB1	10 % PA6F	-
EBA 4	Mix1	90,5% EBA	4,5% CB1	5 % PA6F	-
EBA 5	Mix1	98,5% EBA	1,5% CB1	-	-
EBA 6	Mix1	97% EBA	3% CB1	-	-
EBA 7	Mix1	93,4% EBA	6,6% CB1	-	-
EBA 8	Mix1	90% EBA	10% CB1	-	-
EBA 9	Mix2	95% EBA	5% CB1	-	-
EBA 10	Mix1	95% EBA	5% CB1	-	-
PBT 1	Mix12	95% PBT	5% CB1	-	-
PE 1	M1	95% LLDPE	5% CB1	-	-
PE 2	M2	95% LLDPE	5% CB1	-	-
PE 3	M3	95% LLDPE	5% CB1	-	-
PE 4	M4	95% LLDPE	5% CB1	-	-
PE 5	M5	95% LLDPE	5% CB1	-	-
PE 6	M6	95% LLDPE	5% CB1	-	-
PE 7	M7	95% LLDPE	5% CB1	-	-
PE 8	M8	95% LLDPE	5% CB1	-	-

Table 3 - continued

Material Name	Mix Method	% wt Matrix Material	% wt Cond. filler	% wt Filler	% wt Comp.
PE 9	M1	95,5% LLDPE	4,5% CB1	-	-
PE 10	M1	94,5% LLDPE	5,5% CB1	-	-
PE 11	M1	92% LLDPE	8% CB1	-	-
PE 12	M1	90,5% LLDPE	9,5% CB1	-	-
PE 13	Mix3	98,5% LLDPE	1,5% CB1	-	-
PE 14	Mix3	97% LLDPE	3% CB1	-	-
PE 15	Mix3	95% LLDPE	5% CB1	-	-
PE 16	Mix3	90% LLDPE	10% CB1	-	-
PE 17	Mix4	95% LLDPE	5% CB1	-	-
LDPEc0R1	Mix 5	95 % LDPE	-	5% PA6WF	-
LDPEc1	Mix 5	94,5 % LDPE	-	5% PA6WF	0,5% MAPE
LDPEc2	Mix 5	92,5 % LDPE	-	5% PA6WF	2,5% MAPE
LDPEc3	Mix 5	90 % LDPE	-	5% PA6WF	5% MAPE
LDPEc4	Mix 5	94 % LDPE	-	5% PA6WF	1% MAPE
LDPEc0R2	Mix 5	95 % LDPE	-	5% PA6F	-
LDPEc32	Mix 6	94 % LDPE	-	5% PA6F	1% 3210
LDPEc34	Mix 6	94 % LDPE	-	5% PA6F	1% 3410
LDPA 0	Mix 8	90% LDPE	5% CB1	5% PA6F	-
LDPA 1	Mix 8	89% LDPE	5% CB1	5% PA6F	1% MAPE
LDPA 2	Mix 8	89% LDPE	5% CB1	5% PA6F	1% 3210
LDPA 3	Mix 8	89% LDPE	5% CB1	5% PA6F	1% 3410
LDPA 4	Mix 8	89% LDPE	5% CB1	5% PA6F	1% AX89
LDPA 5	Mix 10	89% LDPE	5% CB1	5% PA6F	1% AX89
LDRF 1	Mix 10	89% LDPE	5% CB1	5% ReF	1% MAPE

Table 3 - continued

Material Name	Mix Method	% wt Matrix Material	% wt Cond. filler	% wt Filler	% wt Comp.
LDRF 2	Mix 10	86% LDPE	5% CB1	7,8% ReF	1% MAPE
LD 1	Mix 8	90% LDPE	10% CB1	-	-
LDPX1	Mix 9	45% LDPE	5% CB1	50% SWE12	-
LDPX2	Mix 9	45% LDPE	5% CB1	50% SWE12	-
LDPX3	Mix 9	68% LDPE	7% CB1	25% SWE12	-
PS1	Mix 9	70% LDPE	5% CB1	25% S 5	-
HD 1	Mix 11	45% HDPE	10% CB1	-	-
HDPX 1	Mix 11	45% HDPE	5% CB1	50% SWE12	-
HDPX 2	Mix 11	45% HDPE	5% CB2	50% SWE12	-
HDPX 3	Mix 11	40% HDPE	10% CB2	50% SWE12	-