THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Electronic Waste Plastics Characterisation and Recycling by Melt-processing

A study of the melt-processing of ABS, HIPS and PP ternary blends in relation to plastics composition and metal contamination analyses from waste electrical and electronic equipment with the objective of facilitating recycling

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Department of Materials and Manufacturing Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2013

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Cover:
Refining and melt-processing of WEEE plastics; as-received flakes (left), contaminant separated and granulated flakes (middle), melt-blended and melt-filtered granules (right).

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Abstract

Melt-processing of blended plastics from waste electrical and electronic equipment (WEEE) is a method to facilitate mechanical recycling, and this might improve the recycling conditions and increase the amounts of plastics being recycled. To ensure the quality of melt-blended plastic waste, it is essential to know the composition of the incoming material and then possibly improve the compatibility between the different polymer phases. WEEE plastic compositions as well as the mechanical and thermal properties obtainable from a model material of a recyclable WEEE plastics blend have been studied in this work.

A real collected and recyclable WEEE plastics fraction was found to contain mainly high impact polystyrene (HIPS, 42 weight% (wt%)), acrylonitrile-butadiene-styrene copolymer (ABS, 38 wt%) and polypropylene (PP, 10 wt%). The remaining part (10 wt%) consisted primarily of other styrene-based thermoplastics and polyolefins. 1-2 wt% were found to be non-thermoplastic contaminants including wood, polyurethane foam and silicone rubber. The amount of merged HIPS and ABS was relatively stable at 80 ± 4 wt% (95% confidence interval) in the sampled waste volume of 600 kg.

Virgin and recycled (containing real collected and sorted WEEE plastics) ternary blends, with the same relative composition of HIPS, ABS and PP as presented above, were blended to model the studied WEEE plastics fraction. Melt-processing by extrusion was compared with injection moulding. An intermediate degree of orientation corresponding to 400-500 % melt-elongation, obtained by extrusion, resulted in the highest ductility while the ductility of the injection-moulded material was significantly lower, but exhibited less variation. The stiffness and yield stress of the recycled ternary blend were found to be higher, while the elongation at break was lower than the values for the virgin blend. It was also seen that the stiffness and the yield stress of the virgin and recycled blends mainly followed the rule of mixtures, but that blending had an adverse impact on the elongation at break, indicating incompatibility between HIPS, ABS and PP. The thermal analysis of the blends indicated relatively low thermo-oxidative stability, with an onset temperature of exothermic oxidation at 187 ^{o}C for the recycled blend and 200 ^{o}C for the virgin blend. The low thermo-oxidative stability indicated that it is necessary to increase the amount of active thermo-oxidative stabilisers. The low ductility of the blends implied the need of improving the compatibility between the plastic phases.

Keywords: WEEE, e-waste, plastics recycling, composition analysis, melt-blending, ternary polymer blend, processing conditions

Preface

This thesis for the degree of Licentiate of Engineering reports work carried out since the summer of 2010 within the group of Polymeric Materials and Composites at the Department of Materials and Manufacturing Technology, Chalmers University of Technology, Gothenburg, Sweden.

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List of Appended Papers

This thesis is based on the work contained in the following Papers, referred to by Roman numerals in the text:

I. **E. Stenvall**, S. Tostar, A. Boldizar, M. R. StJ. Foreman, K. Möller, *An analysis of the composition and metal contamination of plastics from waste electrical and electronic equipment (WEEE)*. Waste Management, Volume 33, Issue 4, 915-922 (2013).

Contribution: Main author, experimental work, evaluation and main part of writing the manuscript.

II. S. Tostar, **E. Stenvall**, A. Boldizar, M. R. StJ. Foreman, *Antimony leaching in plastics from waste electrical and electronic equipment (WEEE) with various acid solutions and gamma-irradiation.* Accepted for publication in Waste Management, 2013.

Contribution: Joint planning, taking part in experimental work and evaluation.

III. S. Tostar, **E. Stenvall**, A. Boldizar, M. R. StJ. Foreman, *The influence of gamma-irradiation on repeated recycling and accelerated aging of ABS.* Manuscript.

Contribution: Joint planning, taking part in experimental work and evaluation.

IV. **E. Stenvall**, S. Tostar, A. Boldizar, M. R. StJ. Foreman, *The influence of extrusion conditions on mechanical and thermal properties of virgin and recycled PP, PS, ABS and ternary blends of them.* Manuscript.

Contribution: Main author, experimental work, evaluation and main part of writing the manuscript.

Contents

1. Background

Plastics in waste electrical and electronic equipment (WEEE) have received interest in recent years due to their increasing volume, their high content of hazardous substances and improper waste treatment, especially in developing countries. Large quantities of WEEE are presently being exported to developing countries, where the waste treatment has been entirely driven by the economic value obtainable from the waste with rudimentary methods [1].

The high content of WEEE plastics (20-35 wt%) means that recycling is important, both to comply with current legislation and to make use of recyclable raw material. There are however challenges to consider in the recycling of WEEE plastics. Firstly, the presence of hazardous additives, traditionally cadmium compounds have been used in pigments and the use of halogenated flame retardants especially in styrene-based plastics is still common practise. Secondly, both the use phase and recycling phase degrade polymers and consume antioxidants, and this may result in unpredictable and insufficient properties of the recycled plastics. Thirdly, the diversity of thermoplastics containing many different additives, contaminants and molecular weight distributions complicates both recycling by blending and plastics separation.

Modern material recovery facilities in developed countries normally employ a high degree of WEEE plastics separation, but the separation technology is expensive, complicated and sensitive to certain types of contamination. To obtain a low degree of contamination in the separated plastics, substantial rest fractions are normally produced. Furthermore, many plastics are difficult to separate from each other due to overlapping properties and the waste plastics property ranges are widened due to many different grades, additives and states of degradation. Against this background, an initial coarse separation followed by simple melt-blending of different plastics offers some advantages, especially in material recovery facilities with the ambition to recycle relatively small waste streams containing many different plastics with limited financial means.

1.1. Objective

The overall objective of the present work has been to facilitate recycling by studying different steps to compatibilise and melt-process blended WEEE plastics. It is expected that melt processing of blended plastics could provide a cost-efficient and straightforward recycling option, and that this might be particularly advantageous in developing countries. The work has focused on the mechanical and thermal properties to evaluate the performance of WEEE plastic blends.

In order to reach the overall objective, to study the recyclability of a WEEE plastics blend, it is of uttermost importance to understand the composition of the WEEE in order to study their recyclability and process optimisation. For this reason, a significant part of this work has been devoted to an analysis of the composition of a recyclable WEEE plastics fraction, which has been compared to two other WEEE plastic fractions that are not directly recyclable. Another initial aim has been to blend and melt process a model material based on the results of the WEEE plastics composition analysis.

The work has not been industry-initiated, but it has benefitted from a close collaboration with many recyclers, recycling equipment manufacturers and recycling experts.

2. Waste Electrical and Electronic Equipment (WEEE) in general

2.1. Introduction

Electrical and electronic equipment (EEE) is defined by the European Union (EU) as appliances using electricity or electromagnetic fields to work properly [2], for instance televisions, cell phones, ovens and electric toys. The discarded EEE is referred to as WEEE or e-waste, where WEEE normally refers to more categories of appliances than e-waste [3]. According to EU, WEEE can be divided into 10 different categories with different recovery and recycling targets presented by the WEEE-directive. The 10 categories together with their recycling targets and fulfilment of the targets (as reported by Swedish recyclers) can be seen in Table 1 [2, 4].

Table 1: WEEE categories and recycling targets according to the WEEE directive compared to the Swedish recycling targets and their fulfilment according to the Swedish environmental protection agency [2, 4].

N:o	Category	EU Recycling Targets (wt%) (2012-2015)	Swedish Recycling Targets (wt%)	Actual Recycling in Sweden (2007)
1	Large household appliances	75	80	92
2	Small household appliances	50	70	85
3	IT and telecommunications equipment	65	75	83
4	Consumer equipment and photovoltaic panels	65	75	95
5	Lighting equipment	50	70	88
6	Electrical and electronic tools (with the exception of large-scale stationary industrial tools)	50	70	33
7	Toys, leisure and sports equipment	50	70	87
8	Medical devices (with the exception of all implanted and infected products)	50	-	78
9	Monitoring and control instruments	50	70	81
10	Automatic dispensers	75	80	13

WEEE has been found to be the fastest growing waste fraction in modern time, already accounting for 8 weight% (wt%) of all municipal waste [5]. Global estimates of WEEE quantities are complicated due to export, insufficient reporting and informal collection of WEEE, but estimates in the range of 20-50 million tons annually have been made [6]. A relatively large portion of this waste has been generated within EU; about 7-10 million tons annually around year 2010 [7-9], which can be compared with the 150 000 tons of WEEE collected in Sweden in 2011 by the national central collection organization, El-kretsen [10]. The total amounts collected in Sweden may seem small in comparison with EU, but the WEEE streams are significant per capita, since more than 16 kg/person annually was collected in Sweden [10], whereas most EU-countries cannot reach the targeted 4 kg/person per annum [7]. The percentage of the collected WEEE reused or recycled is also higher in Sweden (93 wt%) than in any other EU country [11].

The WEEE directive has two main priorities, firstly to prevent the generation of WEEE and secondly to encourage environmentally sound ways of reusing, recycling and recovering WEEE in order to reduce landfilling. Although controlled ways of treating WEEE are encouraged by the WEEE directive and will partly be binding for the EU member states in 2016 [6], large quantities of WEEE are exported from developed to developing countries especially in Africa and Asia [12, 13]. China has become a major importer of both legal and illegal WEEE exports. The imports have been estimated to be 35 million tons annually [14], which is a significant fraction of the WEEE generated globally. The problem with large exports of WEEE to developing countries like China has been found to be the lack of well-equipped treatment facilities and a significant informal recycling sector. In China, 98% of the 700.000 employees working with WEEE are working within the informal sector with simple recycling methods lacking any environmental pollution control [6]. Advanced recycling facilities in China cannot compete with the low investment costs and the ambiguous environmental responsibility of the informal recycling sector, so that the main incentive for WEEE recycling in many developing countries is the short-term profit from the recycling of a few selected materials [6, 15].

2.2. Hazardous Substances

A large percentage of the WEEE plastics have been found to contain hazardous substances, including brominated flame retardants (BFR), chlorine (Cl), cadmium (Cd) and antimony (Sb). In order to restrict the use of some of the hazardous substances, the EU directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) has been enforced to become the law in the member states. RoHS puts a limit to material recycling of WEEE containing more than 1000 ppm lead, mercury, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) or 100 ppm Cd [16].

The BFRs are effective at hindering flame propagation mainly due to the halogens which capture free radicals. The trapping efficiency increases with halogen size, meaning that bromine (Br) is more efficient than Cl, but Cl has also been used in flame retardants [17]. There are over 75 different Br compound families used as BFR, the ones mainly connected to EEE being the PBDE family, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD) [18]. Both TBBPA and HBCDD have been investigated for their potentially hazardous effects and they will possibly be added in future RoHS regulations [16, 19]. Studies indicate that 25-30 wt% of the WEEE plastics contains BFR [5, 20], which complicates the recycling of them. Some BFRs have been found to be persistent organic pollutants (POP) according to the Stockholm convention, including pentaBDE and octaBDE, which are both in the PBDE family (see Figure 1) [21]. The situation is worsened because some BRF, particularly octaBDE and PBB, form highly toxic polybrominated dioxins and furans (PBDD/F) when subjected to thermal stresses, for instance during reprocessing [22]. Even worse is that Sb in the form Sb_2O_3, which is often used as a synergist to BFR, has been found to catalyse the formation of PBDD/F, especially from PBDE [23]. Incineration or even recycling of plastics has the potential to form both PBDD/F due to BFR and sometimes also polychlorinated dioxins and furans (PCDD/F) due to Cl from polyvinylchloride (PVC) or Cl additives. The combined effect of PBDD/F and PCDD/F is not well understood and the number of combinations is huge, but initial studies indicate that the mixed dioxins and furans have a similar or even greater toxicity than PBDD/F or PCDD/F alone [18]. It should be mentioned that studies have been made on ways to separate BFR from WEEE plastics, and the solvent-based technique called CreaSolv®, in which styrene-based plastics are dissolved but not the BFR, has gained most attention [24].

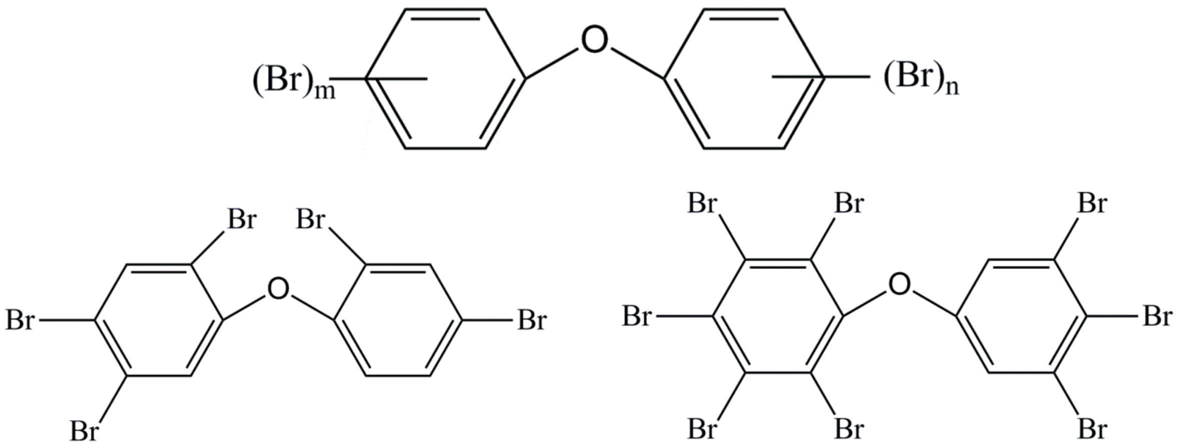

Figure 1: Molecular formulae of generic PBDE (top), examples of pentaBDE (bottom left) and octaBDE (bottom right).

Sb is normally used as Sb_2O_3 to catalyse the polymerisation of poly(ethylene terephthalate) (PET) [25] or as a synergist to BFR [22]. Sb_2O_3 in WEEE plastics is important since it is suspected to be a carcinogen and is listed as a priority pollutant by EU and the United States environmental protection agency [25]. The reason for the interest in Sb_2O_3 is also its ability to catalyse the formation of PBDD/F as well as the scarcity of the remaining raw material supplies of Sb, mainly in China [26].

The use of Cd in modern EEE is rigorously restricted by the RoHS directive [16], but in WEEE the levels of Cd can still be high, partly due to the previous use of Cd in plastic additives. Cd compounds has mainly been used as catalysts in polymerization reactions or as stabilizers in PVC and pigment additives, especially in acrylonitrile-butadiene-styrene copolymers (ABS) [27]. A study of the heavy metal content in television housings has reported high Cd concentrations, even a few per cent being found in one housing [22], which becomes a problem from a safety and materials recycling point of view.

2.3. WEEE Plastics Composition

WEEE has been found to contain 20-35 wt% plastics [5, 28, 29], which makes it important to recycle plastics both from a value point of view and to fulfil the current WEEE treatment targets. Although the percentage of plastics in WEEE is generally high, it is very dependent on the WEEE category. Toys and monitoring and control instruments have been found to contain more than 50 wt% plastics, while lighting equipment and medical devices contain less than 5 wt% plastics [30]. The WEEE plastics consist of many different resins (resin is here defined as all polymer grades that can be associated with a specific generic abbreviation, for instance ABS), over 15 resins being frequently found in composition studies [9, 29]. Figure 2 shows the results of four studies of the composition of WEEE plastics in Europe. The studies are not however strictly comparable since they were performed on differently pre-treated waste streams and on very different amounts. The German and the United Kingdom (UK) studies were performed on small WEEE appliances and were based on 180 kg and 100 kg respectively [28, 31]. The Swiss study was based on the total annual collected WEEE in Switzerland in 2007 (26 600 tons), the polyurethane (PUR) found in this analysis being due to large cooling appliances included only in this study [32]. The Combident study was based on 634 polymer samples provided by five recycling and EEE manufacturing companies, and the results may not be representative of typical WEEE collected in Europe [31].

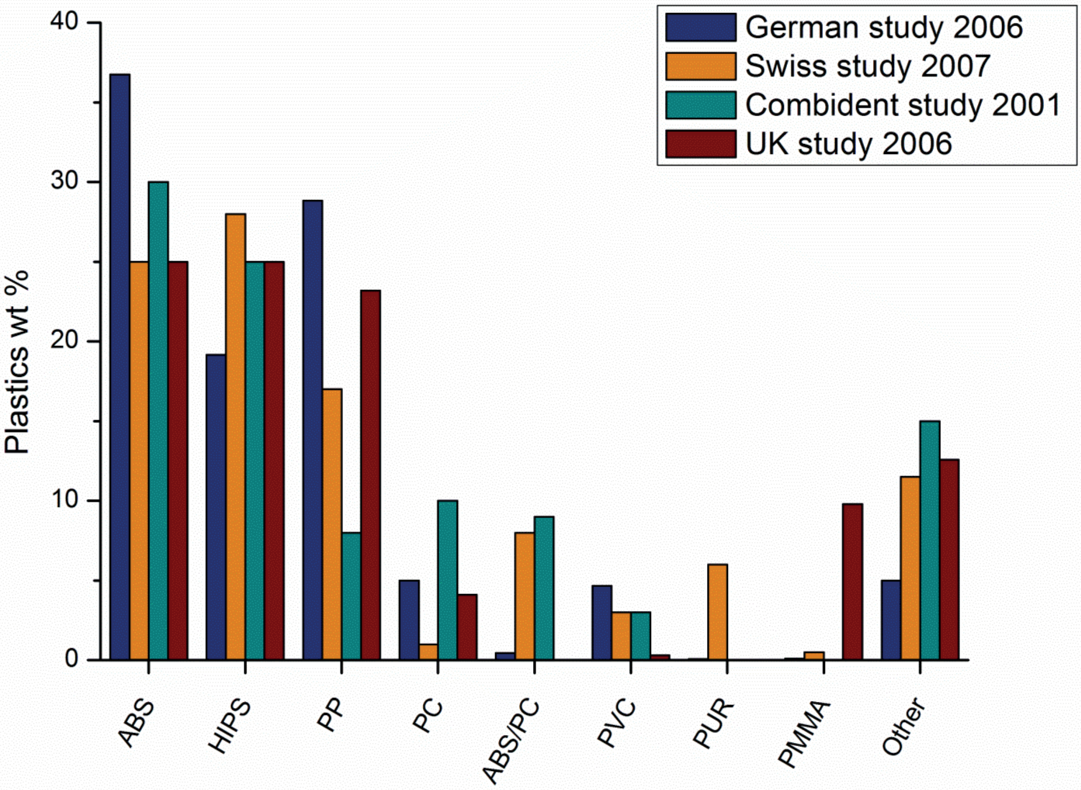

Figure 2: WEEE plastics composition according to different analyses in EU [28, 31, 32].

Most of the resins in Figure 2 are thermoplastic. The results indicate that the major constituents of WEEE plastics are ABS, polypropylene (PP) and high impact polystyrene (HIPS) [28, 31, 32]. All polystyrene (PS) is not impact-modified but is normally not differentiated from HIPS, so they are counted together. HIPS has been found to be the predominant plastic in television housings while ABS is the most common plastic found in computers, computer monitors and printers [9, 20, 33]. Other large constituents (sometimes found at 5 wt% of the total plastics composition in WEEE) are PVC, polycarbonate (PC) and the commercial blend of ABS+PC [28, 32]. Polyphenylene ether (PPE) (same as polyphenylene oxide, PPO) was not found in all composition studies, possibly be due to its miscibility with and similar characteristics to PS. PPE has however been found in relatively large amounts (17 wt%) in plastics from computer housings and to some extent in television housings [20, 34].

2.4. WEEE Plastics Collection and Recycling

Many countries have adopted or are considering the adoption of an extended producer responsibility (EPR) system for WEEE. The principle of EPR is to make the original equipment manufacturers (OEM) responsible for the recycling/recovery of the products they put on the market. It is notable however that EPR makes the OEMs responsible for the recovery but not for the collection of waste [15]. In some countries, like Sweden, there have for a long time been national recovery systems and central organizations coordinating both the collection and WEEE treatment to appointed material recovery facilities (MRF) [4].

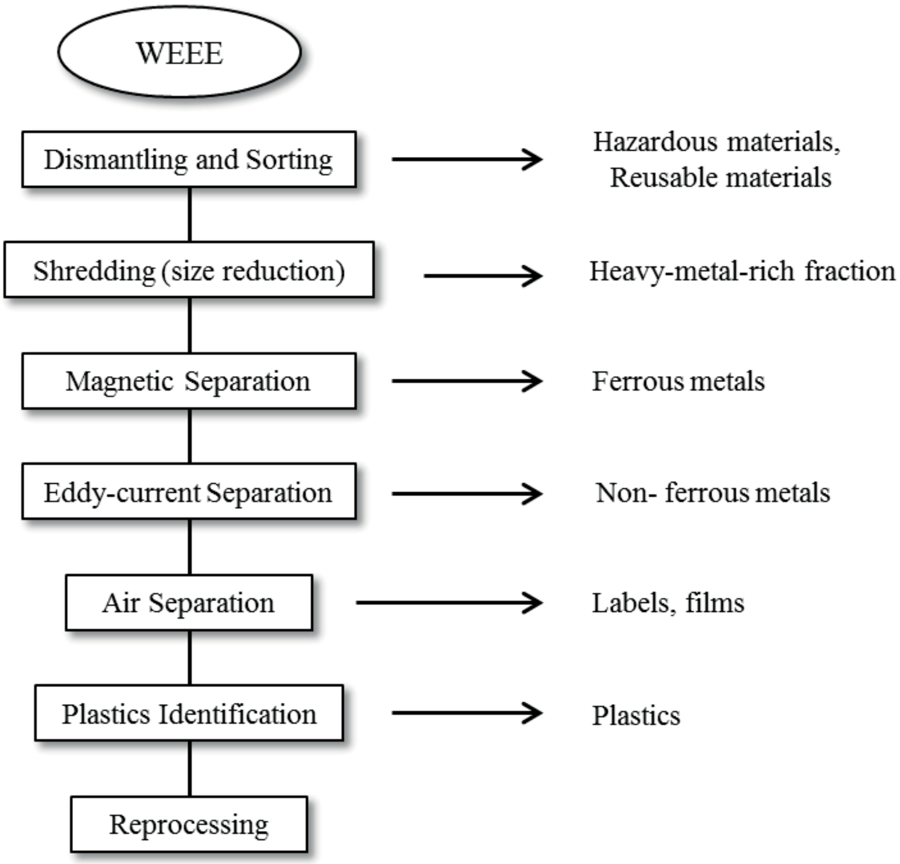

Figure 3: Schematic of a principal recycling process of WEEE in an MRF [29, 35].

Normally WEEE treatment in an MRF involves recycling/recovery under controlled conditions, often in developed countries. There are two main recycling routes for WEEE plastics, either mechanical recycling (recycling without influencing the polymer length substantially) or chemical recycling (recycling by depolymerisation). Chemical recycling involves the degradation of polymers to low molecular weight products that can be reused in fuels or as raw materials in the generation of new polymers [29, 36]. Mechanical recycling (focused in this work) instead involves component recovery, pre-treatment, size reduction, separation and the reprocessing of waste, which can be performed in many different ways depending on the specific MRF. Figure 3 indicates some of the more commonly performed processes in an MRF and the output materials obtained from the processes. Initially reusable, valuable or even hazardous components are sorted out from the main WEEE stream [35]. Some products, like cathode ray tubes, fluorescent lamps, refrigerators and freezers, require special treatment facilities and are also sorted out initially if they are mixed with other WEEE [37]. Metal remaining after magnetic and eddy-current separation can be separated from plastics by vibration systems or by electrostatic separation [38, 39]. Plastics identification is often performed by density separation, infrared radiation sorting, x-ray transmission sorting or triboelectric separation [39, 40]. Multiple sorting steps are usually required to obtain single plastic resin fractions with a relatively low level of contamination. The identification and separation of different plastics is however complicated by the many different plastic resins used in EEE, the small property differences between the plastic resins and the huge number of grades and additives causing a wide range of properties even in plastics based on the same resin. This results in an expensive, time-consuming and complicated WEEE plastics separation process leaving relatively large residual fractions. The complicated recycling process is also indicated by the fact that only a minor fraction (less than 25 wt%) of the WEEE plastic fraction is recycled globally [35]. For all these reasons, the focus of the present work has been to investigate the possibility of blending different plastic resins to facilitate the recycling process.

The discussion above mainly refers to material recycling under controlled conditions, but as described in chapter 2.1, significant amounts of WEEE are being recycled in developing countries under rudimentary conditions, often involving manual steps to disassemble WEEE with hammers, screwdrivers and with bare hands [35]. Acid leaching with aqua regia to extract gold from circuit boards and the dumping of cathode ray tubes in the open air are examples of WEEE treatments reported from developing countries [1]. It has been reported that plastics, especially from large WEEE appliances are sorted manually with colour matching before being reprocessed, without any care of hazardous substances in the plastics. Most of the plastics are however deemed to be unrecyclable due to impurities seen by the naked eye or the difficulty of separating them or lack of matching colours. Often the unsorted plastics are landfilled or burnt in open fires [1].

3. Polymer Blending and Degradation in general

3.1. Polymer Blending and Compatibilisation

Polymer blends have gained a lot of interest in society. Already in 2002 about 36 wt% of the total polymer consumption consisted of blends and the percentage has been increasing [41]. The advantages of blending polymers are usually improved properties at a low cost and easier plastics recycling [41, 42]. The idea of recycling by blending is simple, but it is complicated by the poor compatibility between different polymeric resins, often resulting in a dispersed microstructure with weak interfacial adhesion between the phases [43].

The miscibility of polymers follows to a large extent the saying; “like dissolves like”, which is expressed in the equation of the free energy of mixing (ΔG_{mix}) (see Equation 1) [44].

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

A negative Gibb’s free energy of mixing is a necessary requirement for a homogeneously miscible polymer blend. Since the gain in entropy (ΔS_{mix}) is negligible for long polymer chains, the free energy of mixing can only be negative if the heat of mixing (ΔH_{mix}) is negative. This implies that for polymers to be miscible the mixing should be exothermic, which is normally not the case unless there are specific interactions between the blended polymers, for instance hydrogen bonding or dipole-dipole bonding [42]. A model of ΔH_{mix} has been proposed and has been used widely in polymer science (see Equation 2), but with the drawback that it does not take into account any specific interactions and thus assumes $\Delta H_{mix} \geq 0$.

$$\Delta H_{mix} = \mathrm{V}(\delta_A - \delta_B)^2 \varphi_A \varphi_B \qquad (2)$$

The total volume of the blend (V) and the volume fractions of the polymer resins (φ_A, φ_B) are always positive, but the model proposes that a blend with large differences in the volume fractions is more likely miscible. ΔH_{mix} is dependent mainly on the difference between the solubility parameters ($\delta_A - \delta_B$) of the two polymer resins [44]. The solubility parameters of polymers can only be determined indirectly and they are affected by, for instance, the number of cross-links and chain branches along the polymer backbone. The solubility parameter of a polymer must therefore be regarded as very approximate or applicable only to a very specific grade [45]. Approximate solubility parameters have been calculated or have been indirectly determined in many different ways for PS (15.6-21.1 MPa$^{0.5}$) and PP (17.2-19.2 MPa$^{0.5}$) [45], although the widths of the ranges are substantial, they do overlap. The widths of these solubility parameter ranges are associated mainly with different measurement techniques and calculations, but for the resins in the WEEE plastics the ranges can also be expected to be wide due to diversities of the grades and states of degradation within each polymer resin.

Based on the thermodynamic considerations of mixing, three types of blends can be distinguished; miscible, partially miscible and immiscible. Miscible blends exhibit only one glass transition temperature (T_g) and are typically homogeneous in the nanometre scale [42].

A known example of a blend which is miscible over a wide range of temperatures is PPE with PS [41, 46]. In partially miscible blends, small parts of the polymeric resins are dissolved in each other and the blend exhibits two T_g:s, but shifted towards each other. Normally the blended resins exhibit similar solubility parameters and, although two phases are present, the interphase region is wide and the interfacial adhesion good. Many blends of ABS+PC are partially miscible [42, 47]. Most polymer blends are however immiscible, exhibiting coarse phase morphologies and sharp interfaces between the blended resins. To enhance the performance of immiscible polymer blends by improving the interfacial adhesion and dispersion of the blended resins, compatibilisation is needed [42, 43].

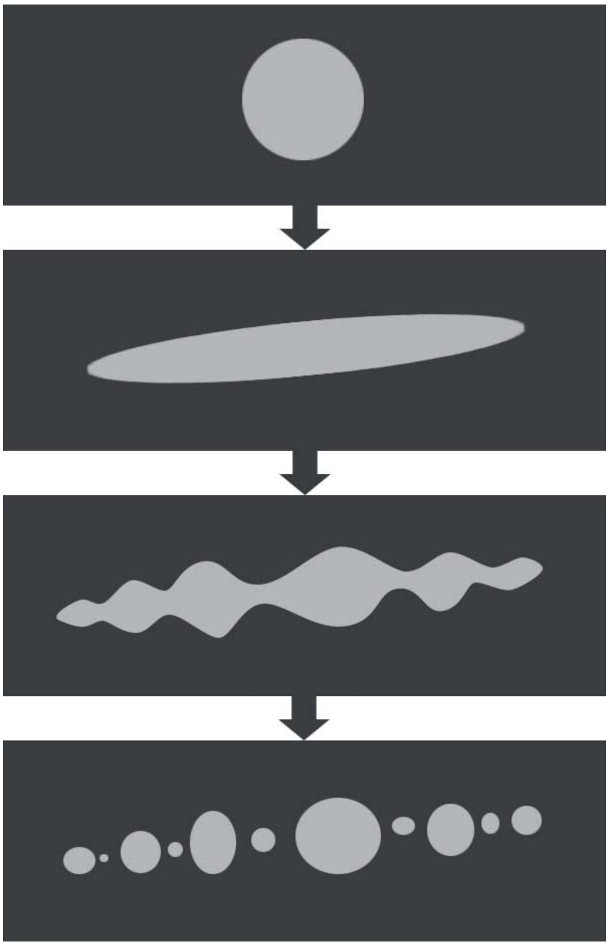

Figure 4: Schematic model of droplet break-up in a flow field.

Two morphologies are frequently seen in binary immiscible polymer blends, 1) a co-continuous two-phase morphology, 2) a dispersed morphology with one low volume fraction polymer phase dispersed in the matrix of the other polymer phase [42]. The phase inversion concentration between a co-continuous and a dispersed morphology has been found to be at roughly an average volume fraction of 0.19 ± 0.09 for several blends, but it depends on the strain and thermal history of the blend [41, 48]. The actual shape, size and distribution of the phases in the blend are the result of a complex interplay between the viscosities of the phases, the interfacial properties, the blend composition and the processing conditions. A dispersed phase in the matrix of another phase normally forms almost spherical drops unless subjected to a flow field in which the droplets become elongated with a greater surface area. As long as the deforming stress (σ) on the droplets is greater than the interfacial tension (γ) tending to conserve the spherical shape, the droplets continue to elongate and eventually become sensitive to interfacial disturbances (Rayleigh disturbances) and break-up into several small drops, as shown in Figure 4 [42, 49]. The capillary number (Ca) defined in Equation 3 controls to some extent the drop deformability and break-up.

$$Ca = \frac{\sigma * R}{\gamma} \tag{3}$$

Large deforming stresses (σ) and large droplet radii (R) result in a larger Ca, and when Ca is above a certain critical number (Ca_{crit}) the droplets break-up or form long stable fibrils. In general for $0 < Ca/Ca_{crit} < 0.1$ no droplet deformation occurs and for $0.1 < Ca/Ca_{crit} < 1$ droplets deform, but do not break. For $1 < Ca/Ca_{crit} < 4$ droplets deform and break-up, while for $4 < Ca/Ca_{crit}$ long stable fibrils form [50]. For dispersed phase morphologies, fine phase dispersions are normally preferred due to the enhancement of mechanical properties [43]. Although a fine phase dispersion may be achievable by optimisation of the processing conditions, it may not remain due to the coalescence of droplets once the deforming stresses disappear [42].

Compatibilisers have three main functions; 1) the suppression of droplet coalescence, 2) the reduction of the interfacial tension and thus increasing Ca [51], 3) increase polymer interface adhesion. Different theories have been proposed to explain the suppression of coalescence, for instance the compression of compatibilisers between two approaching droplets, which would reduce the number of possible conformations of the chains and in this way generate an elastic repulsion between the droplets, shown in Figure 5 [52]. A partial cross-linking of one of the phases is also expected to stabilise the dispersed morphology [41]. Compatibilisers usually have a blocky structure, as can be seen in Figure 6. The copolymer compatibilisers contain at least two blocks, each block being miscible with at least one polymer resin in the blend. The reduction in interfacial tension can then be understood from the surfactant ability of the copolymers [42]. Pre-made blocky copolymer compatibilisers added to the blend are sometimes referred to as physical compatibilisation, whereas the in-situ generation of copolymers in the blend is referred to as reactive compatibilisation [41, 42].

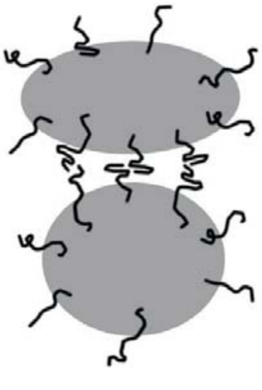

Figure 5: Suppression of coalescence of droplets in a polymer matrix by the compression of compatibilisers [52].

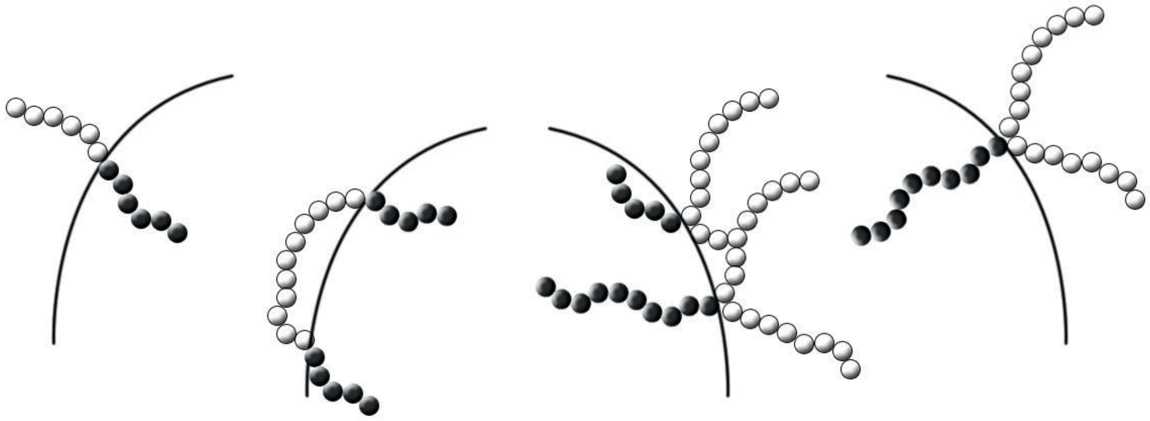

Figure 6: Copolymer compatibilisers from left to right; diblock, triblock, multiple graft and single graft copolymers.

The three main polymeric resins in WEEE plastics have been found to be ABS, HIPS and PP. Different blend compositions of these have been studied, especially binary blends of ABS+HIPS, HIPS+PP, ABS+PP. PS have been found to be miscible with many other polymers, of which the mentioned blend of PPE+PS is the most known. In addition, PS has been found to be miscible or partly miscible with other ethers, polycarbonates and acrylate polymers [41]. It has been found that ABS+HIPS blends are relatively compatible, although not miscible. In fact, one study reports that ABS+HIPS blends exhibit migration during injection moulding, and that the less ductile ABS then forms a skin around the core of the test-bar containing more HIPS [53]. On the other hand, ABS+HIPS blends have been found to exhibit a common T_g, which follows Fox equation for different blend compositions [54]. Most mechanical properties of HIPS+ABS have been reported to follow the rule of mixtures, impact strength being the exception [53-55]. Only 10 wt% HIPS contaminating ABS reduces the impact strength to 50% [55]. A slight synergy could also be seen for the modulus of elasticity (E). A 50:50 composition of ABS+HIPS exhibited a higher E than either ABS or HIPS [54]. HIPS+PP blends are immiscible, and most mechanical properties are lower than would be expected from the rule of mixtures if not compatibilised [56, 57]. Several pre-made compatibiliser systems have been suggested and investigated for HIPS+PP blends, including ethylene vinyl acetate copolymer (EVA) and styrene-butadiene-styrene copolymer (SBS), but the most promising results have been found with styrene-b(ethylene-co-butene)-b-styrene copolymer (SEBS). The advantage of SEBS can be attributed to the styrene blocks being miscible with HIPS, and EB blocks being miscible with PP [56]. A relatively high additions of SEBS of around 15 wt% appears to substantially improve the elongation at break (ε_B) and the impact strength but, since SEBS is a thermoplastic elastomer, higher contents also result in a lower tensile strength and a lower flexural modulus [56, 57]. Few studies have investigated ABS+PP blends, but one study reports that the tensile and flexural strength are lower than would be expected from the rule of mixtures of an uncompatibilised blend. On the other hand, the impact strength of ABS was on the other hand reported to benefit from blending with PP [55], perhaps because of the skin-core effects seen in injection moulded ABS+PP specimens, where an ABS rich skin is formed around a PP-rich core [58].

3.2. Polymer Degradation

The avoidance of excessive degradation of polymers is one of the key challenges in the recycling of WEEE plastics. Consequently low exposure to high temperatures and shear forces is normally strived for in recycling [54]. Polymer degradation and the associated radical formation can be initiated by several mechanisms; thermal, radiation-induced, catalytic and bio-degradation [59, 60]. Thermal degradation may be particularly important in the recycling of plastic blends due to the elevated temperatures when the polymers are melted, in particular the high mechanical stresses during processing locally induces very high temperatures [60]. Polymer degradation refers to all types of irreversible chemical changes in the polymers, but thermal and oxidative degradation normally includes chain scission, depolymerisation (unzipping), carbonisation and side-group reactions [61]. Cross-linking of polymer chains is also a possible consequence of the thermal degradation.

The thermal and thermo-oxidative degradation of polymers having aliphatic carbon main chains can be described by the free radical chain reaction theory illustrated in Figure 7 [61]. Free radical initiation by chain scission could theoretically occur at a random site along the main chain of a perfectly linear polymer, by breaking a C-C bond with an activation energy (E_α) of about 350 kJ/mol. Polymers generally start to degrade at lower temperatures than would be expected from this high E_α, due to weak link sites [62]. Such weak link sites lower E_α and can be found in the vicinity of carbon double bonds, in head-to-head configurations and in peroxide structures in the chain [61, 62]. Macroradical initiation need not be the result of chain scission, but may also be due to hydrogen abstraction. Tertiary carbon atoms in PP or at branched structures are more susceptible to radical formation than secondary carbons [59]. Once the weak link sites are consumed, the degradation is instead shifted to random chain scission with an effectively higher E_α [62, 63]. The propagation step in Figure 7 is also the principle for vinyl polymerisation by addition. Chain scission may then follow intermolecular or intramolecular chain transfer, of which intramolecular transfer is seen in Figure 7. The E_α of the transfer depends on the C-H bond of the abstracted hydrogen, since tertiary, allylic and benzylic hydrogens require less energy [61]. Termination may occur by two radicals forming inert products or by inhibition with heat stabilisers (antioxidants) [59].

Heating polymers in oxygen-containing atmospheres results in thermo-oxidative degradation. In the presence of oxygen the E_α of the polymer degradation initiation is much lower than in an inert atmosphere. Thermo-oxidative degradation starts at about 100 ^{o}C and the initiation E_α is not much more than 100 kJ/mol [61, 62]. The kinetics of hydrocarbon oxidation follows the mechanisms described in the free radical chain reaction theory. The oxidation of hydrocarbons leads to the formation of peroxide radicals followed by hydrogen abstraction and the formation of hydroperoxides [59]. The hydroperoxides have a low thermal stability and tend to decompose into two new radicals at temperatures above 210 ^{o}C in a reaction called chain branching [61, 64]. Although termination may occur as previously described, the decomposition of hydroperoxides has the potential to rapidly increase the number of radicals and significantly degrade the polymers unless it is inhibited by antioxidants [59].

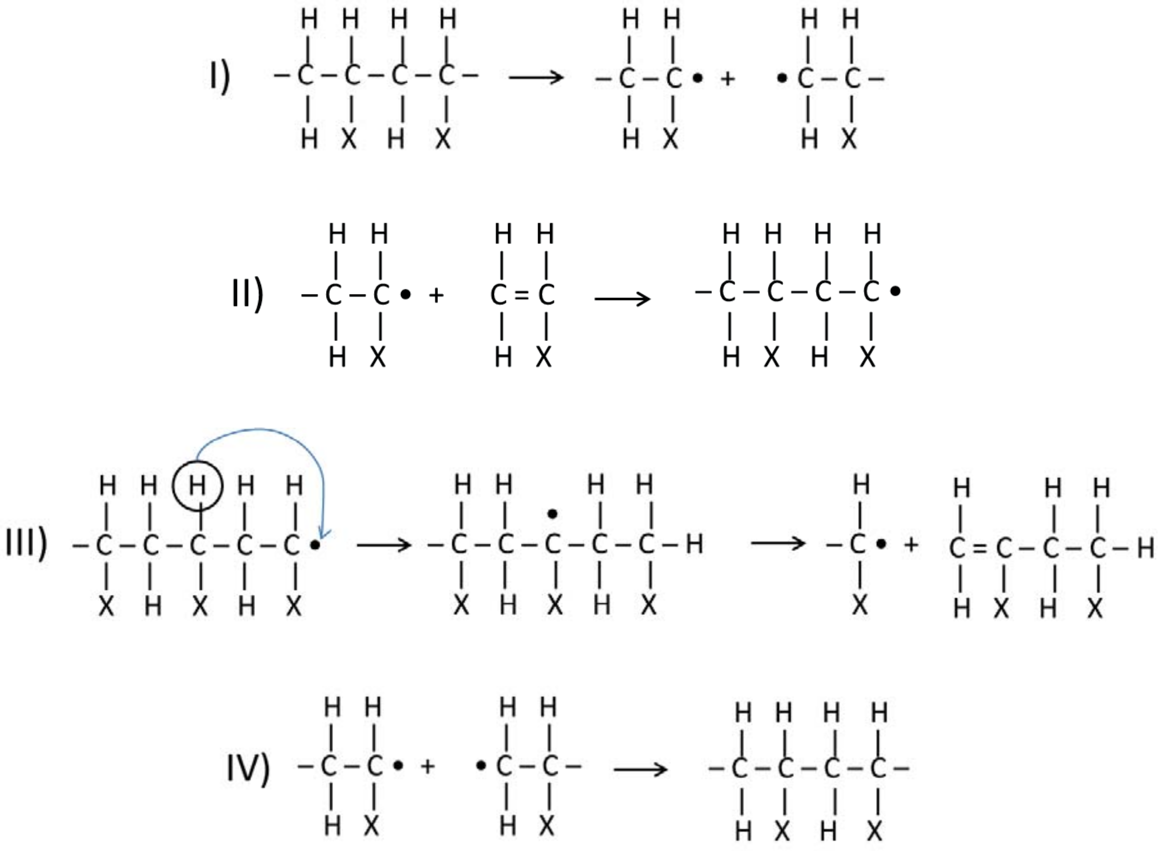

Figure 7: The principles of the free radical chain reaction theory, including; I) Initiation, II) Propagation, III) Intramolecular chain transfer followed by beta scission, IV) Termination by combination [61].

There are two types of antioxidants which either terminate the radical chain reactions (primary antioxidants) or decompose the hydroperoxide groups formed (secondary antioxidants) [65]. Primary antioxidants are usually hindered phenolics or secondary aromatic amines. They act as a donor of hydrogen atoms and react with the propagating radicals to interrupt the oxidative chains [59, 65]. Secondary antioxidants react with hydroperoxides to form non-radical products. Unlike primary antioxidants they are decomposed by the reaction with hydroperoxide rather than containing it [65]. The antioxidants presented have a sacrificial role since when they are consumed the oxidation rate becomes similar to that of the inhibited polymer [59]. For this reason, the amount of antioxidant remaining in recycled material is often important for the mechanical properties and many studies have shown that adding antioxidants prior to recycling may improve the properties [65-67].

The susceptibility to thermo-oxidative degradation differs between polymers. PS is known to be relatively stable towards thermal oxidation with a single decomposition process between 250 and 400 ^{o}C [63]. The stability is due partly to the bulky phenyl group which, it has been suggested, may protect the hydrogen from oxidative attack by steric hindrance [59]. On the other hand, this stability and decomposition above 250 ^{o}C has not been reported for the thermo-oxidative degradation of HIPS and ABS, which can be attributed to the rubber phase in these thermoplastics [68, 69]. It has been shown that the unsaturated polybutadiene (PB) in ABS is a weak link for the initiation of thermo-oxidative degradation, both by thermal activation and by radiation [60, 70, 71]. The thermal degradation mechanisms in PP and polyethylene (PE) are similar and involve mainly random chain scission, but the degradation of PP does not involve any branching or cross-linking which might occur in PE [60]. An interesting characteristic of the initial oxidation of both PE and PP below their melting temperature is the accompanying increase in density, which is believed to be due to a secondary crystallisation which occurs when a few chains undergo chain scission [59]. Incompatible blends of PS with PE or PP have been observed to yield polyolefins with lower thermal degradation temperatures, which has been explained by a radical transfer from PS to the polyolefins [60].

3.3. Repeated Recycling

The degradation of plastics may be regarded as the sum of all the aging effects to which the plastic is subjected during its total life cycle [69]. A total life cycle could include only a manufacturing processes and a product use phase, but it could also include a recycling step followed by another manufacturing step and another product use phase. Evidently repeated recycling and aging of plastics lead to a deterioration in the molecular structure which affects the mechanical performance. Accelerated aging, to simulate the degradation during the use phase, can be achieved in many different ways. Accelerated aging at elevated temperatures in air or nitrogen atmospheres have been studied [68, 69] as well as aging as a result of UV-radiation [72].

Although the degradation of plastics is related mainly to a deterioration in the mechanical properties, a more optimistic viewpoint would be that some mechanical properties worsen while others improve [43]. Repeated recycling and aging of ABS have reported that E and the tensile strength are unaffected or even slightly improved while ε_B and impact strength deteriorate significantly with increasing number of reprocessing cycles [73, 74]. Pérez et al. found that the thermal properties of ABS (including the degradation initiation temperature and the T_g of the styrene-acrylonitrile and PB phases) were practically unaltered after 10 recycling and aging cycles [72]. Boldizar and Möller on the other hand, found that the thermo-oxidative degradation temperature (T_{ox}) of ABS decreased almost continuously with combined recycling and accelerated aging cycles, which was explained by the consumption of heat stabilisers in the material [69]. Scaffaro et al. reported that two repeated recycling cycles did not affect the viscosity of ABS, but that the third cycle reduced the viscosity [74]. Several repeated recycling studies have been performed on ABS [69, 72-74], the interest might be due to difference in the characteristics of the PB rubber compared with the styrene-acrylonitrile (SAN) polymer. Most changes in ABS with respect to recycling and aging cycles have been attributed to the degradation of the SB, resulting in free radical formation and subsequent cross-linking [69, 72-74]. Bai et al. also suggested that the loss of small volatile molecules affects the properties of ABS during the initial reprocessing cycles [73].

4. Materials and Experimental Methods

4.1. WEEE Plastics Composition

A summary of the materials and experimental methods used to study the composition of the WEEE plastics is presented below. A more extensive description can be found in Papers I and II.

The recyclable WEEE plastic fraction was obtained from Stena Technoworld in Halmstad (2011-07-05) and is referred to as Stena 1. 14 samples were taken in succession from a falling stream within a time period of 3 hours and they contained on average 90 flakes each. Stena 1 was a low density plastic fraction and could be regarded as recyclable due to its low content of BFR. A second fraction of slightly higher density was also obtained from Stena Technoworld in Halmstad (2011-01-12), and is referred to as Stena 2. Three samples were obtained by the coning and quartering sample splitting method [75]. The last of the studied WEEE plastic fractions was obtained from Sims Recycling in Katrineholm (2011-05-23) and is referred to as Sims. Three samples were taken from a falling stream. Table 2 summarises the number of flakes, average flake sizes and number of detected materials in these three WEEE plastic fractions.

Table 2: Summary of flake sizes and amounts of analysed materials in the three investigated WEEE plastic fractions. The average flake weight is given together with the standard deviation.

WEEE plastic fraction	Number of samples analysed	Number of flakes analysed	Average flake weight (g)	Different materials detected
Stena 1	14	1226	1.9 (0.3)	29
Stena 2	3	340	1.0 (0.1)	25
Sims	3	230	5.3 (0.5)	31

The samples from all three fractions were washed with water and dried prior to the analysis of the plastics composition presented in chapter 5.1. The characterisation was performed by spectral peak interpretation with fourier transform infrared spectroscopy (FT-IR) of single flakes.

The metal content in the WEEE plastics was studied for samples from all the three WEEE plastic fractions and is presented in chapter 5.2. The investigated metals were either expected to exist in significant concentrations in the plastics (Al, Ca, Cu, Fe and Zn) [76, 77] or could be considered as hazardous substances (As, Cd, Ni, Pb and Sb) [35]. In order to extract metals from the plastics, they were subjected to nitric acid leaching for 20 hours. The influence of the leaching time on the extraction of Al, Cu, Fe, Mg and Zn can be seen in Figure 8. The extraction of Cu, Mg and Zn was independent of the leaching time whereas the concentration of Al and Fe increased with time, but eventually levelled off. It was suggested that 20 hours leaching was a good compromise also for Al and Fe. The metals extracted by the leaching agent were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results of the analyses at Chalmers were compared with those from a complete decomposition of the plastics by wet ashing in a mixture of sulphuric and perchloric acid followed by ICP-OES analysis at MEDAC Ltd. In addition, x-ray photoelectron spectroscopy (XPS) was used to study elements in melt-blended WEEE plastics from Stena 1, the main purpose was to study metals present and confirm that no Br or Sb could be detected in the recyclable WEEE plastic fraction. A fracture surface of the melt-blended Stena 1 was studied by scanning binding energies from 0 to 1350 eV with a step length of 0.4 eV.

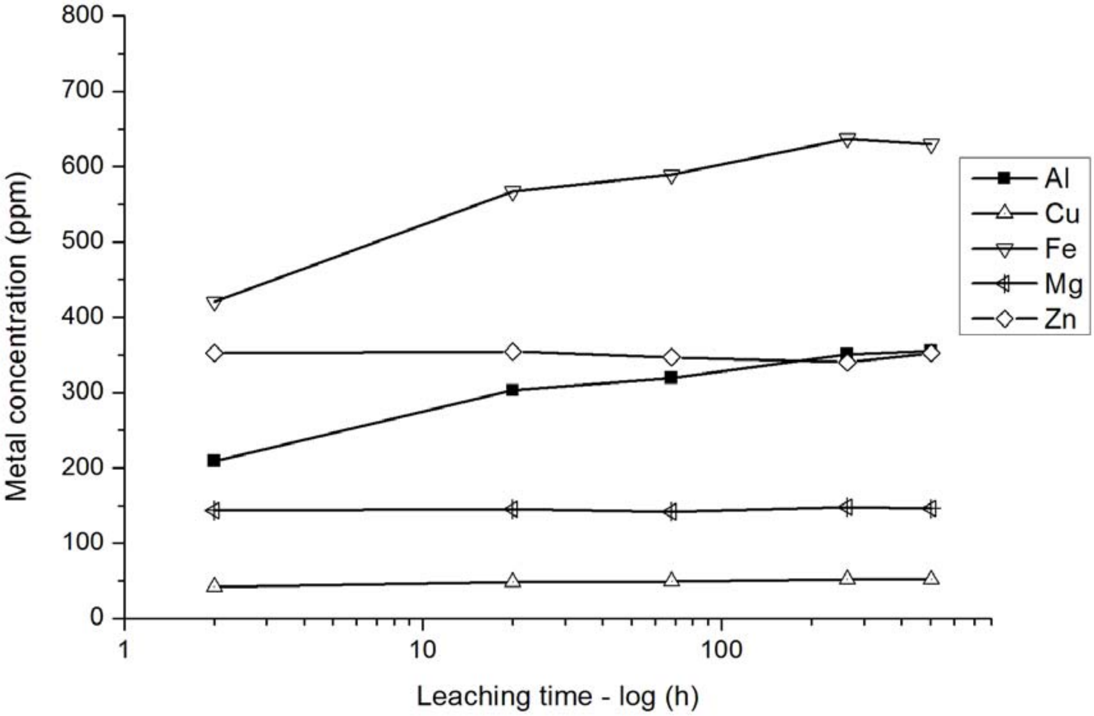

Figure 8: Metal concentration as a function of leaching time with 1 M nitric acid as leaching agent.

The extraction potential of antimony, outlined in chapter 5.3, was studied in one discarded computer housing of flame-retarded ABS. The extraction of Sb was studied by dissolving the ABS by heating in dimethyl sulfoxide (DMSO), using sodium hydrogen tartrate as leaching agent. The Sb concentration was then analysed by ICP-OES. C, H and N levels were studied by CHN elemental combustion analysis, while Br was studied by oxygen flask combustion followed by titration, Sb was analysed by acid digestion followed by ICP-OES. The three last characterisation tests were performed at MEDAC Ltd.

4.2. WEEE Plastics Blending and Degradation

A summary of the materials and experimental methods used in the study of the mechanical and thermal properties of the virgin and recycled ABS, HIPS, PP and their ternary blends is presented below. A more extensive description can be found in Papers III and IV.

The three most common resins found in the WEEE plastics fraction were ABS, HIPS and PP, and these were studied as single materials and as blends. The three commercial virgin polymers used were; Terluran GP 22 (ABS), Polystyrol 495F (HIPS) and Moplen EP 240 P (PP), all of which are commonly used in EEE. These resins were blended to a composition of 47 wt% (HIPS), 42 wt% (ABS) and 11 wt% (PP). This virgin ternary blend (TBV) corresponded to the composition of a real recyclable WEEE plastics fraction, as reported in Paper I. In addition, three recycled, sorted and RoHS-compliant WEEE plastic fractions of ABS (purity 99% according to the supplier), HIPS (purity 98% according to the supplier) and PP (purity 96% according to the supplier) were provided by Wertstoffe GmbH & Co. KG. They were studied as single materials and blended to a ternary blend of recycled plastics (TBR), of the same composition as TBV. Terluran GP 35 (ABS) (with mechanical properties similar to those of Terluran GP 22) was used to study the influence of repeated recycling, accelerated aging and gamma irradiation on ABS.

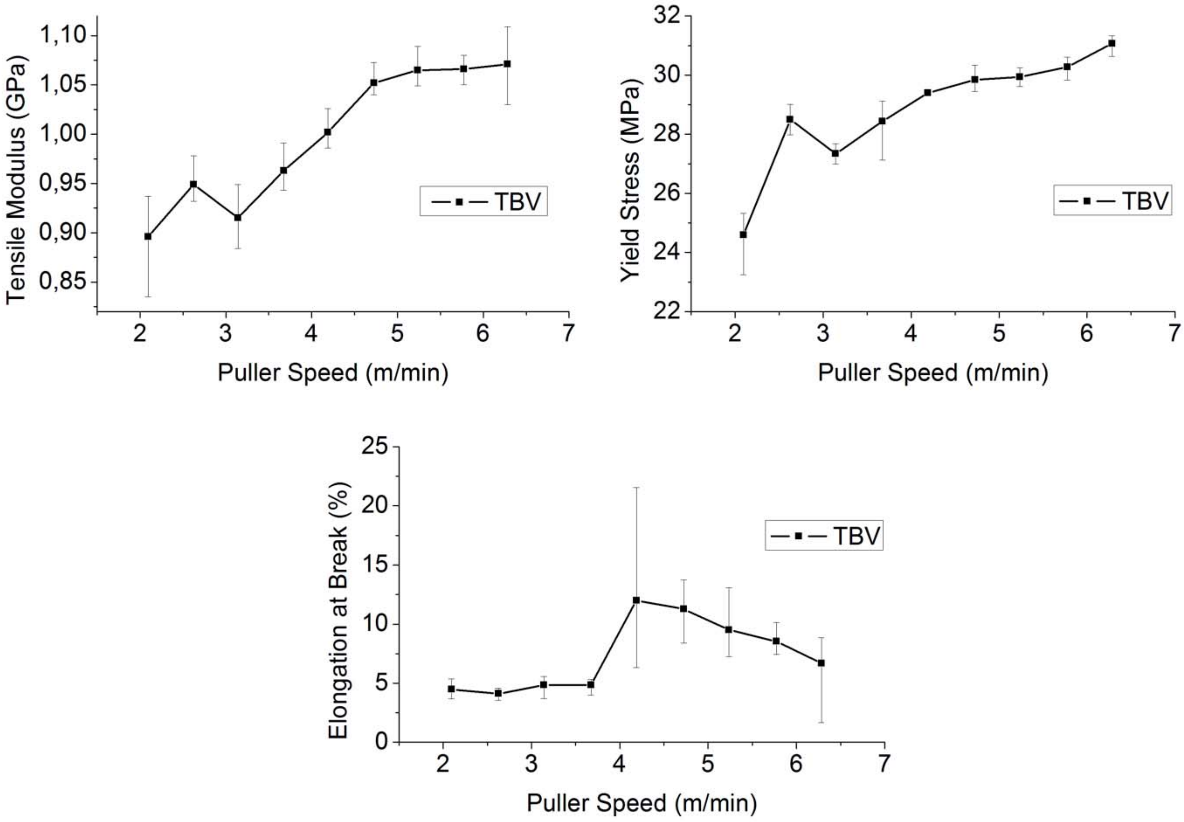

Figure 9: The influence of puller speed on E, σ_y and ε_B of TBV processed at 50 rpm with a 180-200-200-210-210 ^{o}C temperature profile.

The melt-processing of all the materials was performed using a single screw extruder. The screw rotation rate was varied between 20 and 100 rpm and the cylinder zone temperatures were varied between 160 and 260 ^{o}C in order to study the influence of processing conditions on the mechanical properties especially of TBV. The influence of pre-drying the blends prior to melt-processing was studied, but no significant differences in the short-term properties were observed, so pre-drying was not employed except for ABS prior to repeated recycling. Molecular orientation and flattening of the extruded strips were achieved by roll-pulling. Different ratios of the puller speed to the extruder throughput rate, here called the draw-down ratio (DDR), were studied to find its influence on the mechanical properties. Figure 9 show the influence of DDR on E, yield stress (σ_y) and ε_B. As expected the values of E and σ_y increased with increasing DDR, while the ε_B had the highest values and also largest variation for a DDR between 4 and 5. As a compromise, a DDR value of 4.4 was used in the subsequent work. Specimens were punched out from the extruded strips for mechanical and thermal analyses.

Injection moulding (Arburg Allrounder 221M 250-55) of tensile specimens of a geometry (ISO 37-2) similar to that of the extruded specimens was performed on TBV. The combination of melt-blending the material in the extruder followed by injection moulding was also studied.

ABS was subjected to repeated recycling (up to 5 cycles) and accelerated aging between the reprocessing steps in order to model a service time of two years between each recycling. Several repeated recycling studies have been performed on ABS [69, 72-74], but in this case it was used in conjunction with gamma irradiation. Three different specimens were prepared; non-irradiated, irradiated with 40 kGy only prior to the first cycle and irradiated with 10 kGy between each reprocessing cycle.

The mechanical properties of the materials were studied by tensile testing, according to ISO 37-2. The cross-head speed was set to obtain a strain rate of 10% elongation per min for ABS, recycled PP and the blends, 50% elongation per min for HIPS and 200% elongation per min for virgin PP, to obtain rupture times between 0.5 and 5 min, as specified by the standard.

Thermal properties were studied by differential scanning calorimetry (DSC). Transitions were studied by heating in N_2 from 40 to 220 ^{o}C, at 10 ^{o}C per min. Previous studies showed that the thermo-oxidative degradation can successfully be measured and evaluated by the oxidation induction time (*OIT*) and T_{ox} [68, 69]. In this study T_{ox} has been used, and the specimens were heated from 40 to 300 ^{o}C, at 10 ^{o}C per min in an oxygen environment.

Rheological properties of irradiated ABS were determined by capillary rheometry for eight different shear rates (20-1500 s^{-1}). Three different capillary lengths were tested for each material in order to permit a Bagley correction of the shear stress. The shear rate was also corrected by the Rabinowitsch correction.

5. Results and Discussion – WEEE Plastics Composition

5.1. Plastics Composition

The composition of the recyclable WEEE plastic fraction, based on the FT-IR spectral analysis of about 1200 flakes collected from Stena 1, can be seen in Figure 10. The major constituents were styrene-based plastics (84 wt%) and polyolefins (12 wt%). The styrene-based plastics consisted mainly of ABS (also including ABS containing acrylate and ester groups and styrene acrylonitrile copolymers) and HIPS (also including PS containing acrylate and poly(vinyl cyclohexane)). The other styrene-based plastics were polyphenylene ether with styrene butadiene (PPE+SB), styrene methyl methacrylate (SMMA) and ABS+PC. The polyolefins were mainly PP, of which some PP grades were talc-filled, and to a smaller extent PE. The remaining thermoplastics consisted of PVC, PET and polyamide (PA). The thermoplastic elastomer-related materials found were EVA, poly(vinyl butyral), poly(ethylene:propylene:diene) and poly(ethylene:vinyl acetate:vinyl chloride). Roughly 1-2 wt% of non-thermoplastic contaminants was found and this could be of concern in material recycling. The major non-thermoplastic contaminants were wood and paper materials, followed by cross-linked PUR and silicone rubbers. No metals were found, with the exception of one tiny piece of Al foil.

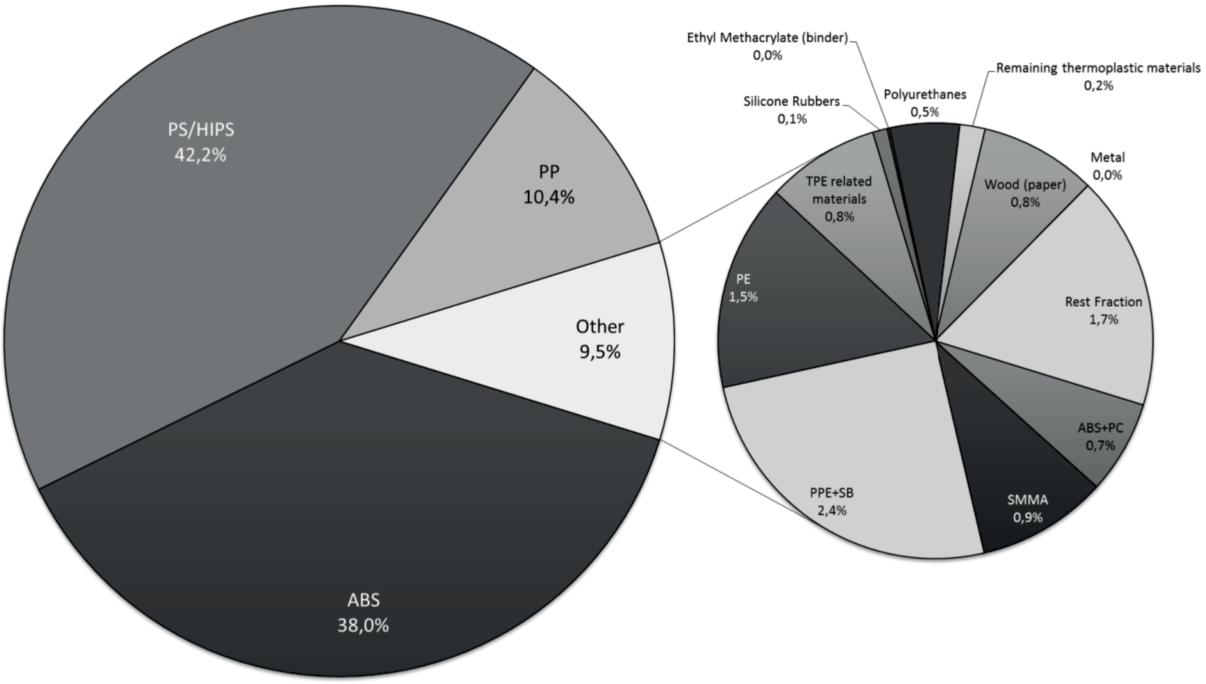

Figure 10: Plastics composition of Stena 1.

Statistics could be calculated for the 14 samples taken in succession from the falling stream of Stena 1 to investigate trends and variations in the composition. The compositions of HIPS, ABS and PP with respect to the sample extraction order are shown in Figure 11- Figure 13. Trend-like behaviours of the compositions were investigated by testing the null hypothesis

(H_0): "the slope of the trend-line equals zero". H_0 has been tested by calculating the standard error (*SE*) (Equation 4) of the trend-line slope (k) from the residual sum of squares of the trend-line and the sample composition points (Equation 5).

$$SE(k) = \sqrt{\left(\frac{RSS}{(n-2) * SXX}\right)} \tag{4}$$

$$RSS = \sum_{i=1}^{n} w_i\big(y_i - (a + kx_i)\big)^2 \tag{5}$$

$$SXX = \sum_{i=1}^{n} w_i x_i^2 \tag{6}$$

n- number of samples
w- weighting factor
a- linear regression intercept on y-axis

According to Hoffmann a t-statistic can be calculated from the k to *SE* ratio to test the null hypothesis [78]. The H_0 hypothesis tested at a significance level of 0.05 could not be rejected for ABS (k = -0.33, *SE* = 0.47), HIPS (k = -0.68, *SE* = 0.65) or PP (k = 0.74, *SE* = 0.39), with the implication that no statistically significant trends in the HIPS, ABS and PP composition could be expected. This conclusion was also supported by the fact that fewer than five successive sample compositions exhibited a trend-like behaviour for ABS, HIPS and PP.

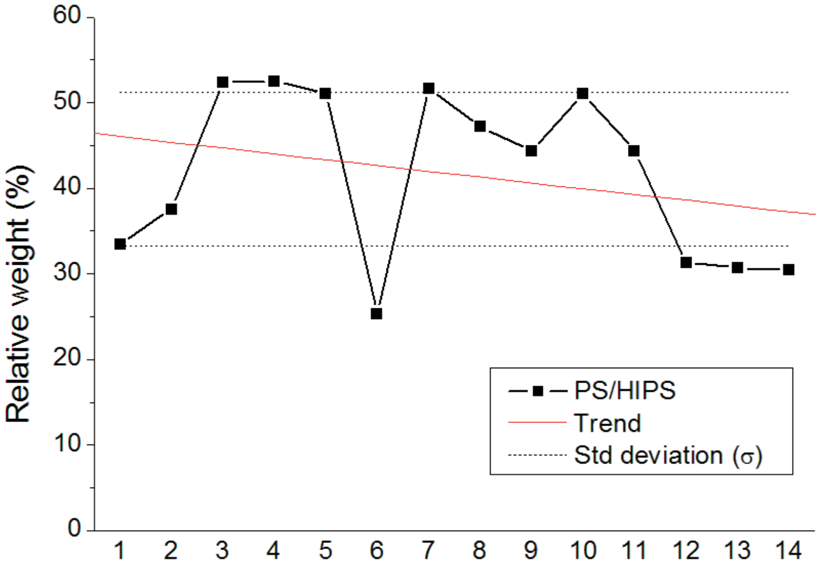

Figure 11: Trend-line of HIPS based on 14 samples taken in chronological order from Stena 1. A hypothesis test of the slope of the trend-line (with significance level 0.05) indicates no significant trend. The dotted lines represent ± 1 standard deviation of the sample mean.

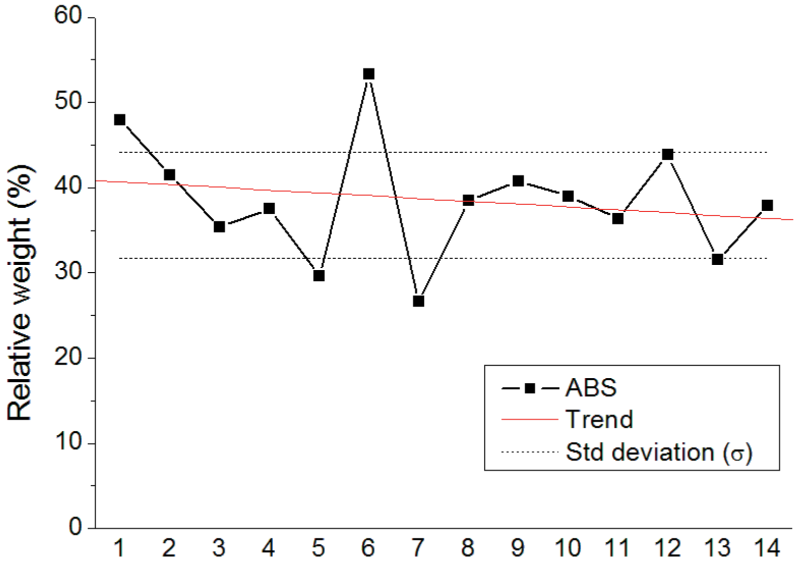

Figure 12: Trend-line of ABS based on 14 samples taken in chronological order from Stena 1. A hypothesis test of the slope of the trend-line (with significance level 0.05) indicates no significant trend. The dotted lines represent ± 1 standard deviation of the sample mean.

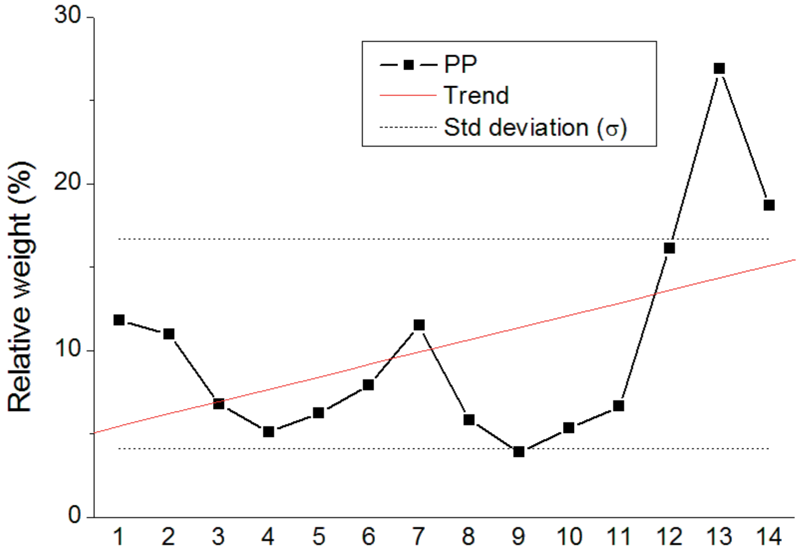

Figure 13: Trend-line of PP based on 14 samples taken in chronological order from Stena 1. A hypothesis test of the slope of the trend-line (with significance level 0.05) indicates no significant trend. The dotted lines represent ± 1 standard deviation of the sample mean.

The material composition distributions have also been tested for normality by the Shapiro Wilk's test using the algorithm described by Royston [79]. The null hypothesis (H_0) tested in this context was formulated: "the composition of material 'X' is normally distributed between the samples". This hypothesis was rejected at a significance level of 0.05 for all the materials except ABS, HIPS and PPE+SB, which can thus be expected to follow a normal distribution. A t-distribution was applied to ABS, HIPS and PPE+SB to calculate a two-sided 95% confidence interval (*CI*) of the mean value of the waste stream composition [80, 81]. The calculated *CI* were, ABS 38.0 ± 3.6 wt%, HIPS 42.2 ± 5.2 wt% and PPE+SB 2.4 ± 0.8 wt%. If the two major plastics, HIPS and ABS, were combined as a single material, the mixture was also found to be normally distributed (with significance level 0.05) having a *CI* of 80 ± 4 wt%. To study the variation in the remaining materials, the coefficient of variation (the standard deviation divided by the mean) was mainly used. It was then found that only ABS, HIPS, PPE+SB, PP and the residual fraction had a coefficient of variation less than 100%, which indicates that the other materials varied a lot between the 14 samples. For the materials present in small amounts, it can however be assumed that the weight of a single flake of that material in one sample has a huge influence on the composition. The coefficients of variation would probably be much less if the materials were granulated into smaller flakes.

Figure 14 shows the composition of the major material groups in Stena 2 and Sims. Stena 1 was added for comparison, although the results for Stena 1 were based on only 14 samples. The styrene-based plastics group was obviously the dominating group in all three waste fractions, but the composition within the styrene-based plastics group differs. HIPS and ABS were the most abundant plastics in Stena 1 and Sims, but the blend of ABS+PC was the most abundant in Stena 2. Stena 2 and Sims also contained large amounts of the other thermoplastics group, mainly PC, PVC, PA, polyoxymethylene (POM) and poly(butylene terephthalate) (PBT). The large amounts of contaminants found in Sims and Stena 2 were notable. It can be seen in Figure 14 that Sims contained glasses, wood materials, thermosetting polymers and metals while the high rubber content might be a major obstacle when considering the recycling of Stena 2.

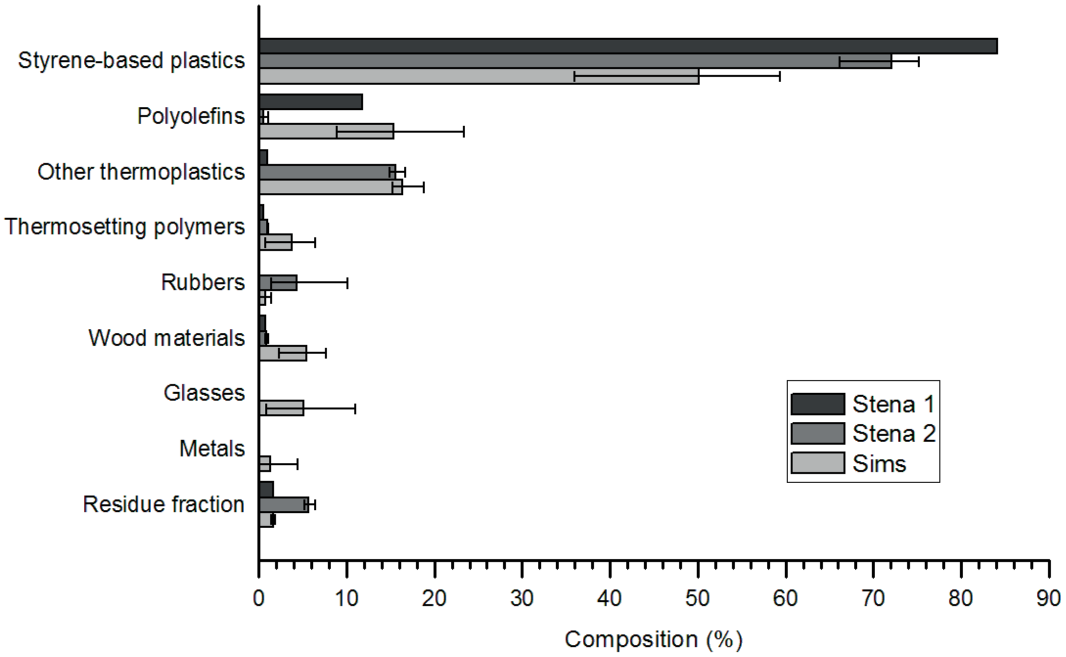

Figure 14: Plastics composition of Stena 1, Stena 2 and Sims. The bars show the variation width of the sample composition of Stena 2 and Sims, no bars were added for Stena 1 because the results were based on 14 instead of 3 samples (as was the case for Stena 2 and Sims).

Stena 1 can be compared with previously reported WEEE composition analyses, summarised in Figure 2. Similar contents of ABS and PP were found for Stena 1 and in the studies presented in Figure 2, but there seems to be a tendency for small WEEE appliances to contain more PP. The contents of HIPS were however higher in Stena 1, which may indicate that a large fraction of the WEEE in Stena 1 comes from television housings and the like. The other European studies found more plastics of higher density (ABS+PC, PVC, PC) than in Stena 1, which is reasonable considering the low density separation performed with Stena 1.

5.2. Metal Content in WEEE Plastics

The metal content of the WEEE plastic fraction was assessed by surface leaching of the plastic flakes and the results were compared with bulk leaching by complete decomposition of the plastics in a wet ashing process at MEDAC Ltd. The results are shown in Table 3. The high and almost identical results for the Ca contents indicate that Ca is mainly found at the surface. The surface leaching also appears to be efficient for Al, Cu, Fe, Ni, Pb and Zn since similar results were obtained in the two studies. The levels of Mg and in particular Cd were however significantly higher when bulk leaching was performed. The five times higher Mg contents could be attributed to the presence of talc ($Mg_3Si_4O_{10}(OH)_2$) seen both in the investigation of some PP flakes by FT-IR and in the XPS spectrum shown in Figure 15. The contents of Cd (70 ppm) found by bulk leaching were not far from the threshold of 100 ppm specified by RoHS [16] and over 10 times higher than the amount found from the surface leaching. Since almost no PVC was found in Stena 1, the source of Cd was attributed to pigment additives. Cd pigments can be expected to be evenly distributed in the flakes and previous studies suggest that surface leaching leaves most Cd in the bulk unaffected [82].

Table 3: Comparison of the metal contents between bulk leaching at MEDAC Ltd and surface leaching at Chalmers, both on Stena 1.

Metal	MEDAC Ltd (ppm)	Stena 1 (ppm)
Al	370	280
Ca	6300	6100
Cd	70	5
Cu	60	50
Fe	880	500
Mg	670	150
Ni	25	20
Pb	80	110
Zn	310	330

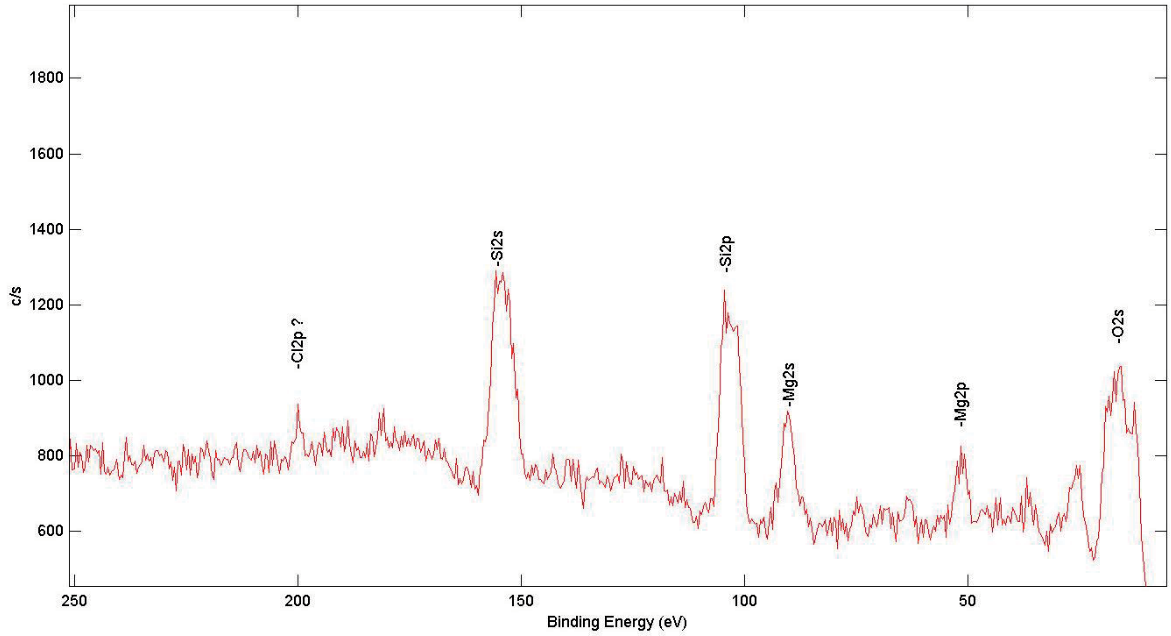

Figure 15: Close-up of the counts per second versus the low binding energy range (0-250 eV) of a survey spectrum (0-1350 eV) from a fracture surface of melt-blended Stena 1.

Figure 16 shows some of the metal contents found in the WEEE plastic samples from the three waste streams studied. Metals that could be considered as hazardous substances (As, Cd, Ni and Sb) were found in low or not-detectable amounts with ICP-OES, with the exception of Pb. Some samples contained 200 ppm levels of Pb, but this was still below the 1000 ppm threshold limit for Pb set by RoHS [16]. Since the amount of Cd found was more than 10 times higher when bulk leaching was performed rather than surface leaching, significant amounts of Cd were present, but these are not shown in Figure 16. The metal content found in Sims was unexpectedly low in comparison with Stena 1 and Stena 2, considering that Sims had the largest amounts of macroscopic metal particles. It is suggested that the macroscopic metal particles in Sims were so infrequent that none were probably present in the leached sample. The high levels of Ca in Stena 1 and Stena 2 can be explained by the calcium carbonate ($CaCO_3$) containing density-separation bath to which the materials have been subjected. It was reasoned that the calcium carbonate would not impede mechanical recycling as the $CaCO_3$ could be used as filler in plastics and scavenge any acidic decomposition products formed during the melt-processing. As Fe and Cu are able to cycle between two oxidation states, they have the potential to catalyse the degradation of polymer chains [83]. This may be a concern in WEEE plastics recycling since high levels of especially Fe were found (500-1000 ppm). Relatively high levels of Zn were also found in the metal analyses and ZnO has been found to accelerate the photodegradation of polyolefins [84].

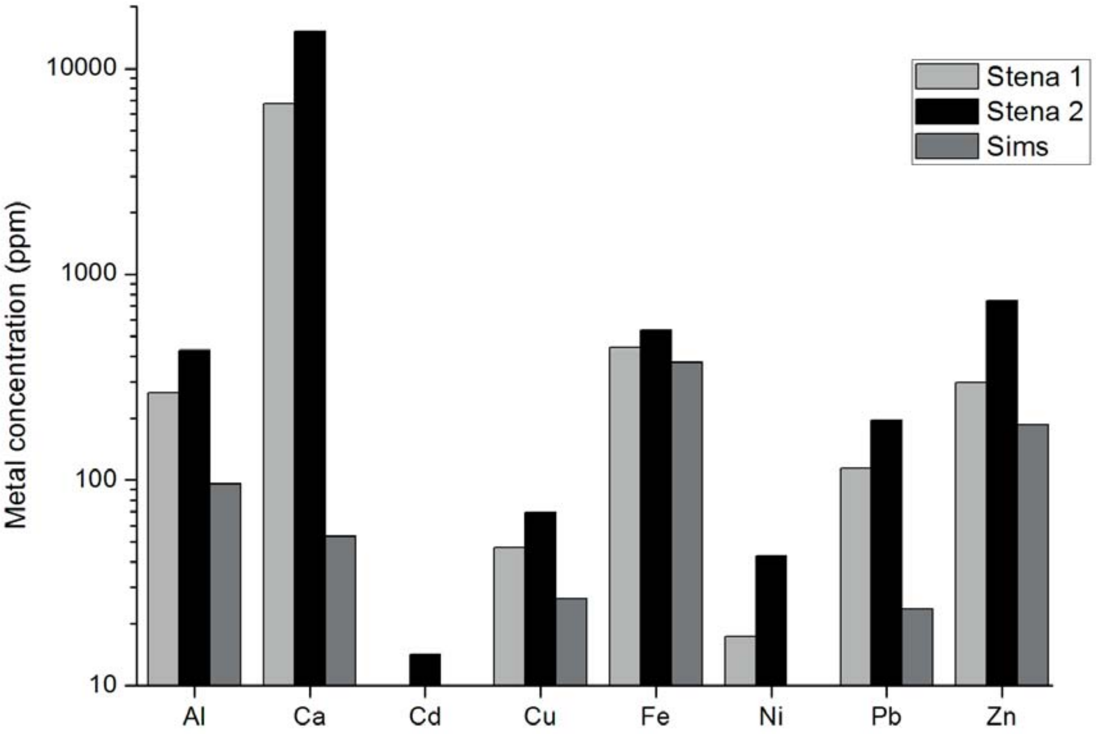

Figure 16: Metal content in Stena 1, Stena 2 and Sims. Found by surface leaching with 1 M nitric acid and analysed with ICP-OES. The Cd concentrations of Stena 1 and Sims, and the Ni concentration of Sims were below 5 ppm.

Although XPS could not provide detailed element analyses, some indicative conclusions could be drawn from the binding energy spectra of Stena 1. C, O and N were easily seen by XPS, as well as a few other elements, but not all the metals found by ICP-OES. The magnification of the low binding energy range presented in Figure 15 shows the presence of Si and Mg, both of which could be attributed to talc ($Mg_3Si_4O_{10}(OH)_2$), but also many other minerals and possibly silicone containing rubbers. If Br or Sb were present in significant amounts they should have been detected, since Br has one and Sb has two prominent peaks in the spectral range studied. This indicates that the recyclable WEEE plastic fraction (Stena 1) contains no or low amounts of Br and Sb. Another interesting observation was that when several survey spectra were made at different positions in a melt-blended Stena 1 sample almost no differences could be seen in the peak heights or positions, which indicates that the melt-blended material is relatively homogeneous, at least within the 100-200 µm range (the smallest area the XPS could resolve with the settings used).

5.3. Antimony Extraction Potential

The results of the elemental analysis of C, H, N, Br and Sb in the ABS computer plastic are shown in Table 4. The N level was attributed to the acrylonitrile groups in ABS. The ratio of Br:Sb was 2:1, which indicates a relatively high level of Sb considering previously reported ratios of 3-4:1 for mixed WEEE plastics [85, 86].

Table 4: Element contents in ABS computer plastic.

Element	C	H	N	Br	Sb
Content (%)	70,8	6,7	4,4	9,6	4,8

Dissolving the ABS plastic by heating in DMSO and then leaching with sodium hydrogen tartrate resulted in the highest Sb extraction yields of the different methods. The tartrate binds to the Sb and forms an anionic complex that can be separated from the plastic with sodium hydrogen tartrate. On the other hand, sodium hydrogen tartrate leaching without dissolving the ABS in DMSO resulted in very low yields of Sb, implying that surface leaching has a low efficiency. Comparing the Sb concentration with the amounts presented in Table 4 indicates that the extraction efficiency of the combined system of DMSO and sodium hydrogen tartrate is approximately 50 %. Similar extraction efficiencies of Sb were found in trials of the Creasolv® process, but the variation in these trials was substantial, between 20 and 50 wt%. The extraction efficiency of Sb was higher for the Centrevap® process, around 60 wt% but, on the other hand, the Br extraction yields were found to be low in comparison with Creasolv® [31].

6. Results and Discussion – Reprocessing Studies on Modelled WEEE Plastics

6.1. Processing Considerations on TBV

TBV was the material in focus when the influence of processing conditions on a model material blend of the WEEE plastics fraction was studied. The screw rotation rate and barrel temperature were considered to be the primary extrusion parameters. Although these two parameters are related, they were varied independently in order to study their influences on E, σ_y, ε_B and elongation at yield (ε_y). Figure 17 shows these mechanical properties as a function of the screw rotation rate. Clearly, the lowest (20 rpm) and the highest (100 rpm) screw rotation rates should be avoided due to the low values of σ_y and ε_y, and a significant standard deviation in ε_B. This might be explained by excessive degradation at low screw rotation rates due to an extended residence time and at high screw rotation rates due to localised heating as a result of the high shear rates.

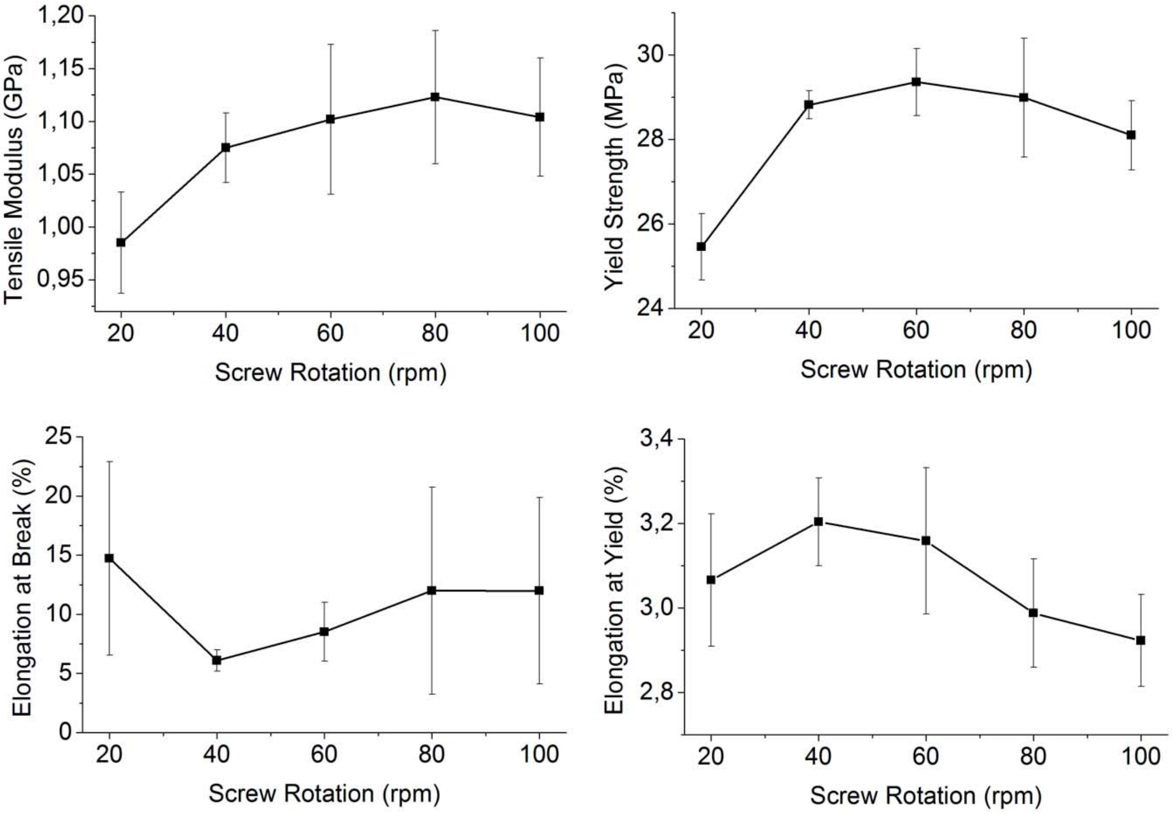

Figure 17: Influence of the screw rotation rate on the mechanical properties of TBV, barrel temperature at 220 °C (straight profile). Error bars represent ± one standard deviation.

Different barrel temperature profiles were investigated. It was found that a straight profile (all zones at the same temperature) yielded the most favourable mechanical properties, although progressive and humped profiles are usually recommended for processing of ABS, HIPS and PP [87]. Figure 18 shows E, σ_y, ε_B and ε_y as a function of the straight profile barrel temperature for three different screw rotation rates. Both σ_y and ε_y tend to decrease with increasing temperature, but no clear trends were discerned for E and ε_B. The 170 – 180 ^{o}C processing range was interesting due to the high σ_y values and favourable ε_B after processing at 60 rpm. Processing at 160 ^{o}C yielded a low ε_B value, which could probably be attributed to insufficient melt-blending. Processing at 260 ^{o}C was observed to result in partial melting already in the hopper and a pulsating output flow of the extrudate.

In all further processing of TBV, TBR and the single material resins, a straight temperature profile was used with a screw rotation rate of 60 rpm. Barrel temperatures of 180, 200 and 220 ^{o}C were frequently used.

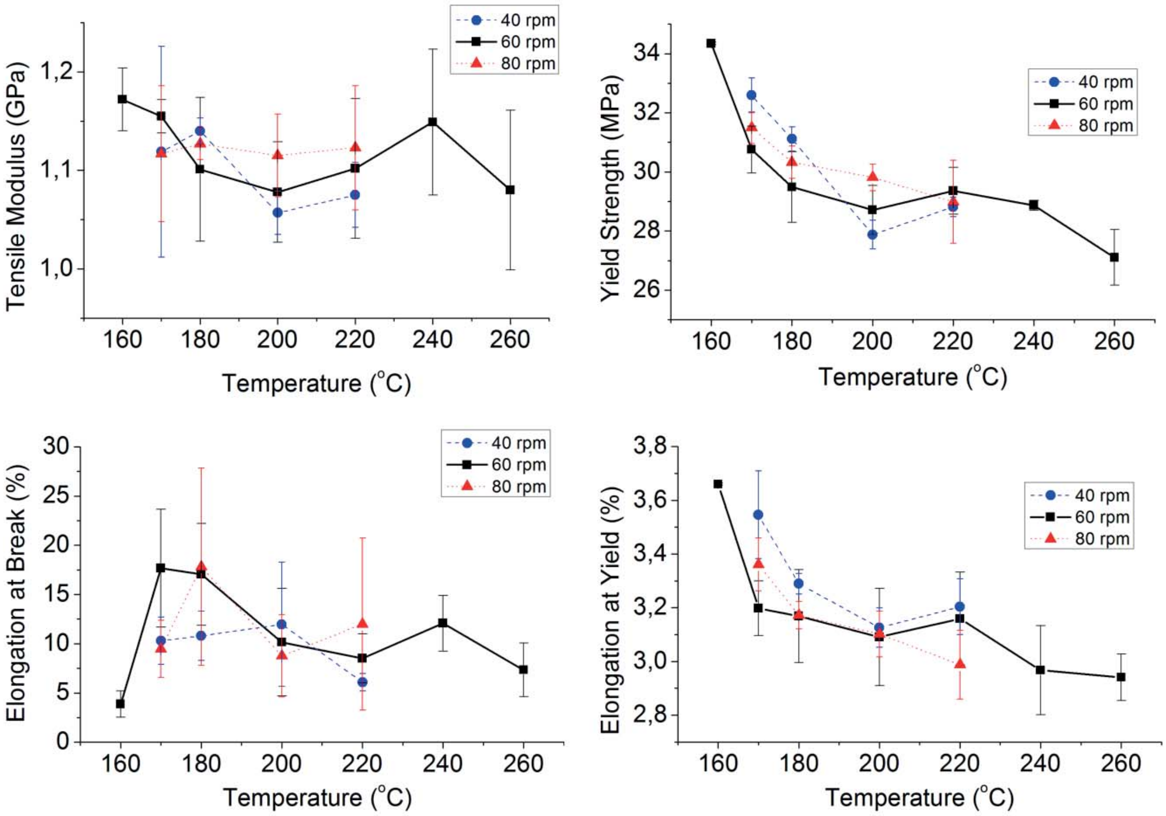

Figure 18: Influence of the barrel temperature on the mechanical properties of TBV. Error bars represent ± one standard deviation.

6.2. Processing by Extrusion versus Injection Moulding

Different melt-processing options for blends are available [41]. In this work, the properties of single-screw-extruded and injection-moulded specimens of TBV at 180 ^{o}C and 220 ^{o}C have been compared. One material that was first extruded and then injection-moulded was also included in the comparison in order to study the combined influence of the processing options. The effects on E, σ_y and ε_B of the different processing options are shown in Figure 19 - Figure 21.

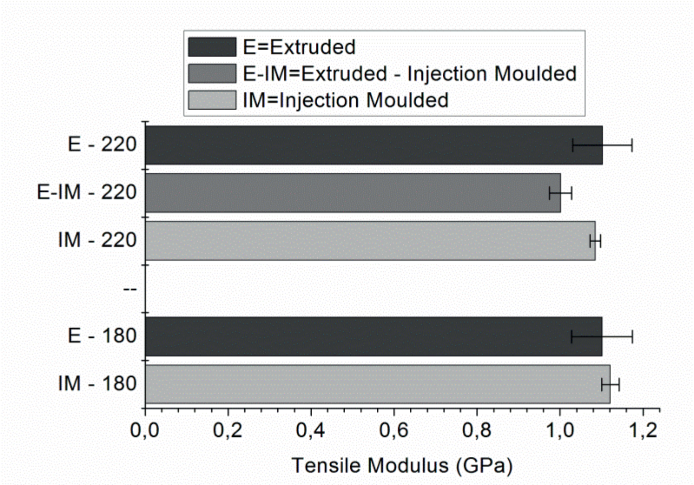

Figure 19: Effects of different reprocessing options on E for TBV. Error bars represent ± one standard deviation.

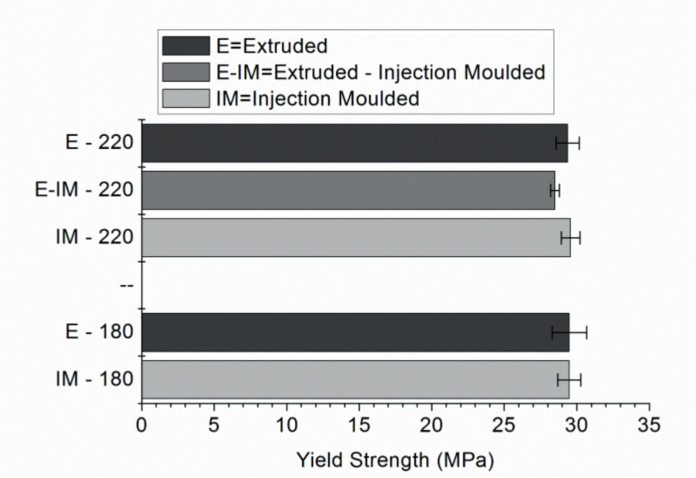

Figure 20: Effects of different reprocessing options on σ_y for TBV. Error bars represent ± one standard deviation.

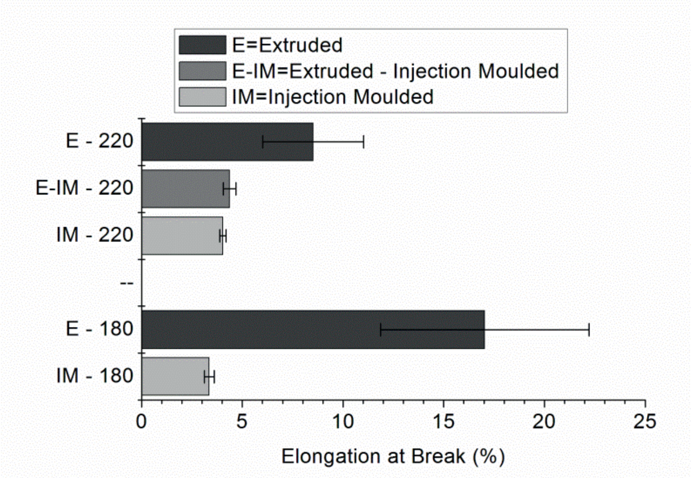

Figure 21: Effects of different reprocessing options on ε_B for TBV. Error bars represent ± one standard deviation.

There was almost no difference in E and σ_y of the extruded and injection-moulded specimens. Combined extrusion and injection moulding yielded lower values of both E and σ_y, which is probably due to increased thermo-oxidative degradation during dual reprocessing. The absolute standard deviation and coefficient of variation of ε_B of the injection-moulded specimens was lower than that of the extruded specimens, seen in Figure 21. An examination of the broken test bars, Figure 22, revealed that the basic layered structure might have been increased by a less ductile ABS forming a skin around a HIPS- and PP-rich core, in a manner similar to that reported by Lindsey et al. [53].

Figure 22: Skin formation on injection moulded TBV specimen.

6.3. Comparison of TBV and TBR

A focus of the work has been to compare the mechanical and thermal properties of the three single materials, ABS, HIPS and PP, with their blends of both virgin and recycled plastics. It was observed that the recycled materials exhibited higher E and σ_y values, but lower ε_B and ε_y values than the virgin materials. The influence of strain rate on the mechanical properties was studied for the virgin single materials and TBV. Varying the strain rate from 0.56 to 140 mm/min resulted in an expected increase in σ_y, but no significant change in ε_B. No ductile to brittle transition could thus be found within the tested range of strain rates.

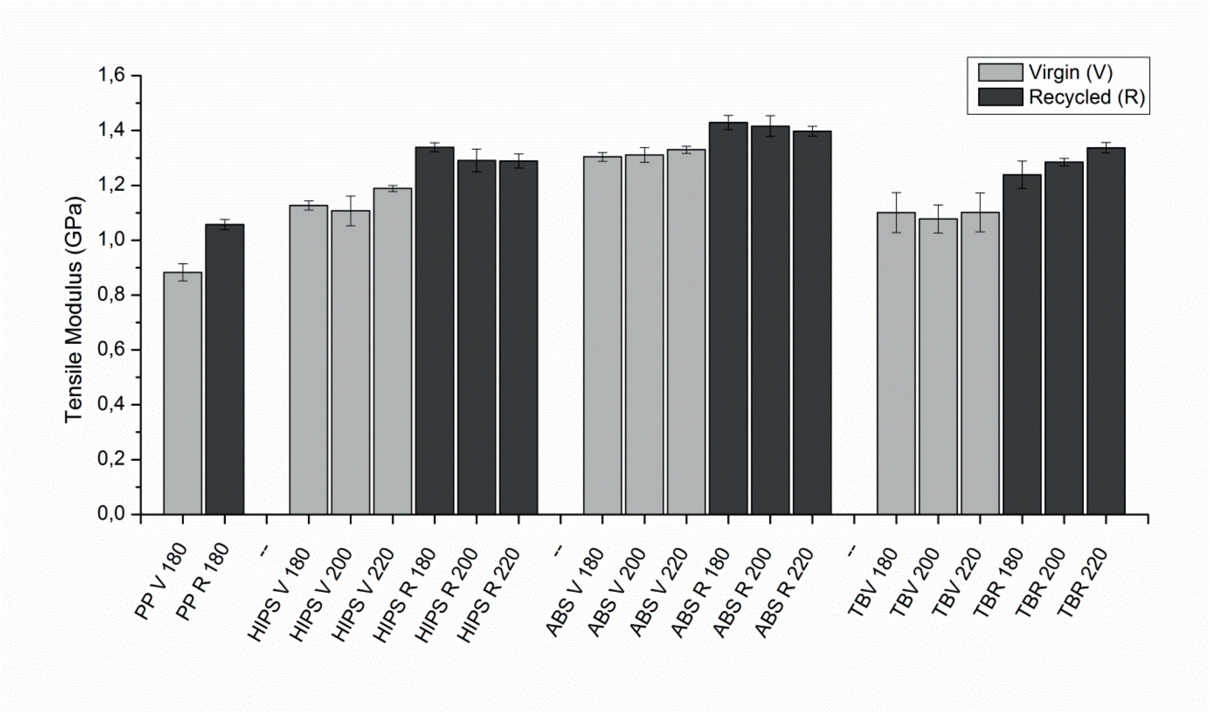

Figure 23: Values of *E* for three single materials; PP, HIPS, ABS and their blend (11:47:42). Error bars represent ± one standard deviation and were based on 7 specimens for all materials except HIPS, for which 5 specimens were used.

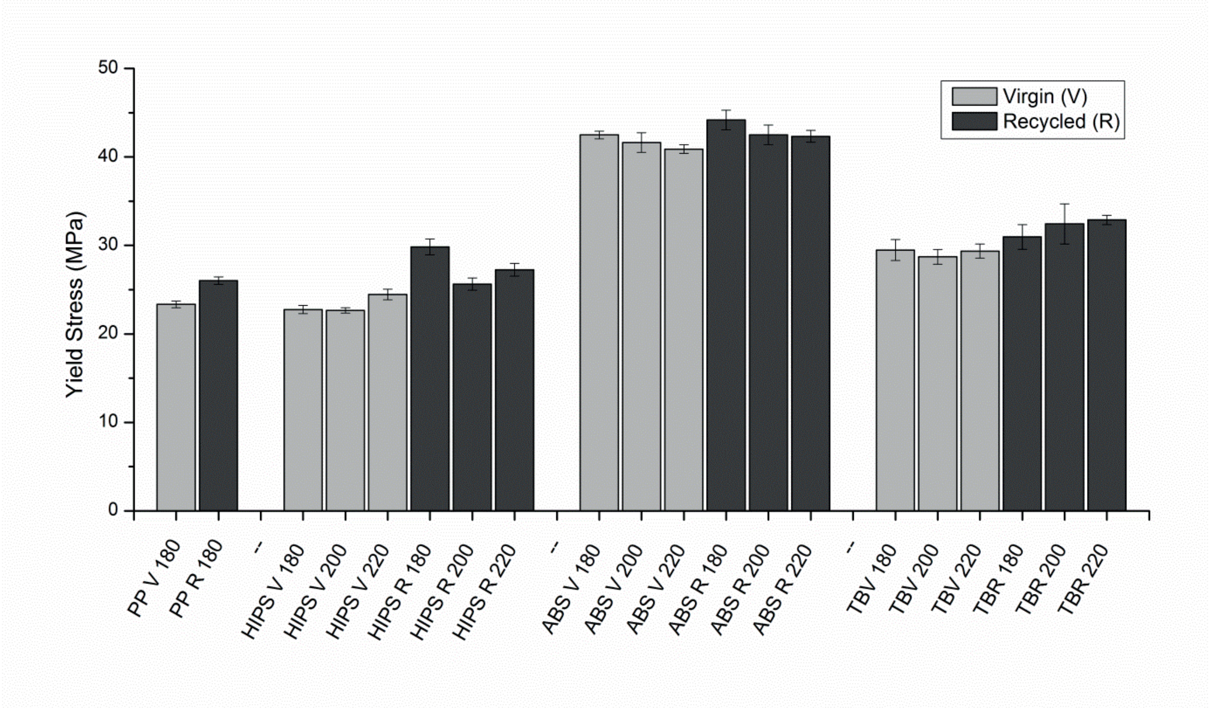

Figure 24: Values of σ_y for three single materials; PP, HIPS, ABS and their blend (11:47:42). Error bars represent ± one standard deviation and were based on 7 specimens for all materials except HIPS, for which 5 specimens were used.

The E and σ_y values for all the materials are shown in Figure 23 and Figure 24. The E and σ_y values of the blends were very close to the expected values from the rule of mixtures, which was in agreement with the tensile properties reported for ABS+HIPS blends [53, 54]. The ε_B and ε_y values for all the materials are seen in Figure 25 and Figure 26. It is evident that the rule of mixtures cannot be applied to ε_B since the values were almost consistently lower for the blends than for all the single materials. It was also notable that there was a slight decrease in ε_B for TBV and TBR when they were processed at higher temperatures. This decrease was also indicated for TBV in Figure 18 when the screw rotation rate was 60 rpm. The standard deviation of ε_B was significant for TBV and TBR as it was for the ABS resin, which indicates that the blends inherit their low ε_B values and relatively large standard deviations from ABS. The large standard deviation may be understood from the random stress-whitening preceding the fracture of ABS and TBV seen in Figure 27. Although the adjacent specimens in Figure 27 were of the same material and had been tested in the same way, the extent of stress-whitening differed considerably. Yielding in ABS occurred at a relatively high strain and stress levels, and this can be expected to result in a chaotic and unpredictable crack propagation [88]. When the standard deviations of ε_B for ABS and the blends were compared with the ε_y values, it was evident that the uncertainties associated with ε_B were related to a post-yielding phenomenon, since they were not seen in ε_y. It was also notable that a few millimetre-sized rubber particles were observed particularly in the ABS extrudate. Their presence might have a detrimental effect on the mechanical properties and they were avoided as much as possible in the tensile specimens.

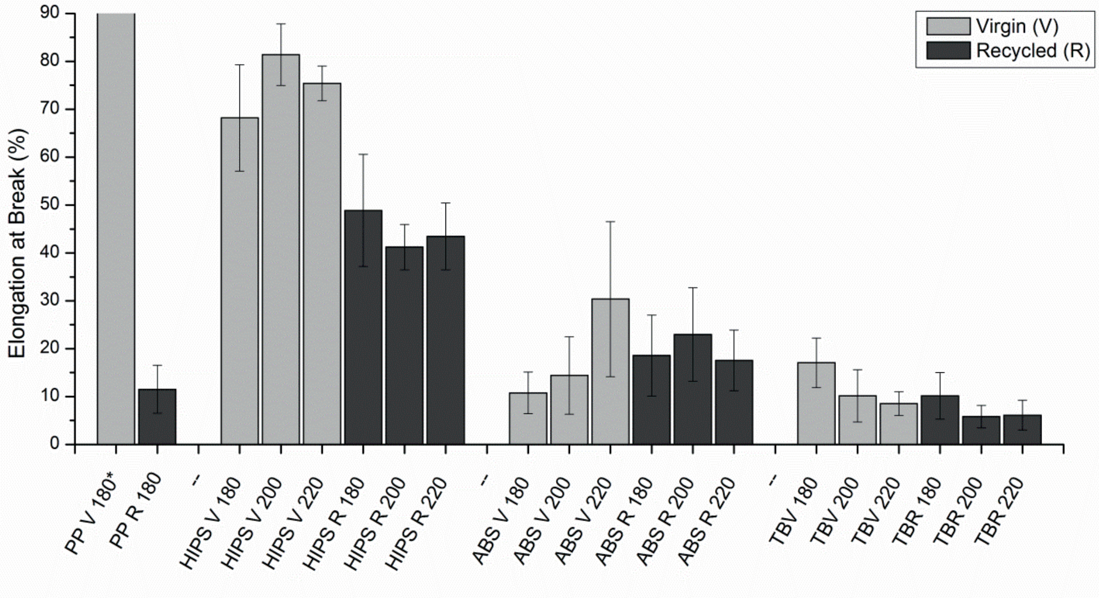

Figure 25: Values of ε_B for three single materials; PP, HIPS, ABS and their blend (11:47:42). Error bars represent ± one standard deviation and were based on 7 specimens for all materials except HIPS, for which 5 specimens were used. * ε_B of virgin PP was 670 ± 70 %.

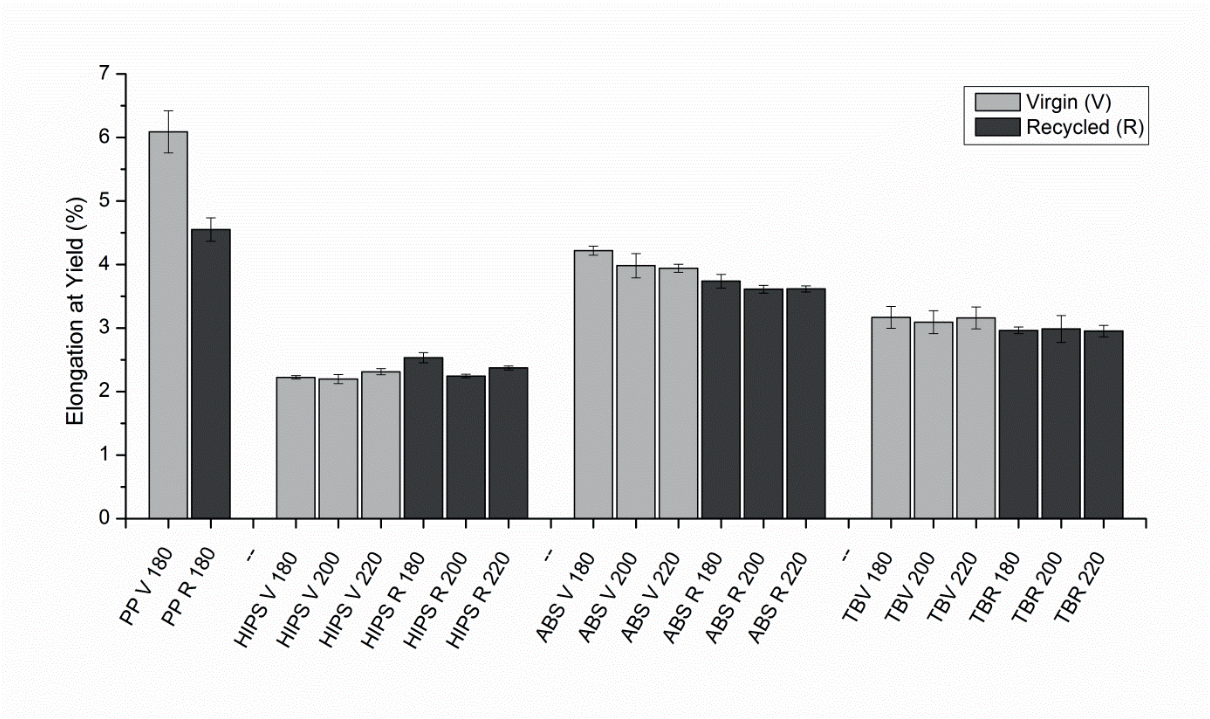

Figure 26: Values of ε_y for three single materials; PP, HIPS, ABS and their blend (11:47:42). Error bars represent ± one standard deviation and were based on 7 specimens for all materials except HIPS, for which 5 specimens were used.

Figure 27: Stress-whitening of tensile test specimens of TBV (two adjacent specimens to the left) and ABS (two adjacent specimens to the right) indicates variation in the extent of stress-whitening prior to fracture of two ABS and TBV specimens tested and processed in the same way.

Table 5 summarizes both the endothermic thermal transitions studied in an inert atmosphere and the exothermic thermo-oxidative degradation studied in air in the virgin and recycled single materials and their blends. The main transitions in the blends and in the corresponding single materials are shown in Figure 28. A small difference was seen in the T_g transition between HIPS and ABS, but only the transition of ABS was clearly seen in the blends. The main transitions of the recycled materials were similar to those of the virgin materials, but it was interesting to find minor transitions also in the sorted recycled materials, as was seen for PP and TBR in Figure 28. Recycled PP contains a clear second melt peak at 129 ^{o}C, which was observed in TBR although PP was a minor constituent in the ternary blend. This peak is characteristic of PE and it has been observed and reported before in separated waste streams of PP [89]. Another transition at 184 ^{o}C was also seen in recycled ABS, probably due to PPE. Since no PPE transition was found in TBR or HIPS it was regarded as miscible with the recycled HIPS, but only partially miscible with recycled ABS. Some PP contamination in both the recycled ABS and HIPS were also seen.

Table 5: Thermal and thermo-oxidative properties of the studied materials. Minor glass transition and melting points indicate smaller transitions with a limited impact on the heat flow.

Thermal Properties	Glass transition (^{o}C)	Minor glass transition (^{o}C)	Melt transition (^{o}C)	Minor melt transition (^{o}C)	Oxidation temperature (^{o}C)	Second oxidation temperature (^{o}C)
PP Virgin			164		224	
PP Recycled			164	129	203	
HIPS Virgin	103				172	
HIPS Recycled	107			165	171	
ABS Virgin	114				207	
ABS Recycled	111	184		165	185	
TBV	114	106	165		200	224
TBR	115	108	164	129	187	219

The onset of the exothermic T_{ox} of the virgin and recycled materials is presented in Table 5. HIPS exhibited the lowest T_{ox}, indicating weak sites of low E_{α}, in this case probably unsaturated elastomers. The T_{ox} of virgin HIPS was notably low considering that it was approximately the same as that of recycled HIPS and significantly lower than that reported in other studies [68]. This indicated a consumed or insufficient heat-stabiliser system in the HIPS grade studied. Both TBV and TBR exhibited two exothermic T_{ox} with a plateau between them, which indicated thermo-oxidative degradation with two E_{α} values probably caused by the chain scission of two different types of weak links. Interestingly it appeared that the thermo-oxidative stability of virgin HIPS was improved when it was blended in TBV, because T_{ox} of TBV was about 30 ^{o}C higher than that of HIPS. It was also noted for TBR that blending had no adverse effect on the thermo-oxidative stability since T_{ox} of TBR was slightly higher than that of its main constituents; recycled HIPS and ABS. In general, all T_{ox} values of the recycled materials were 15-20 ^{o}C lower than that of the virgin materials, except for HIPS.

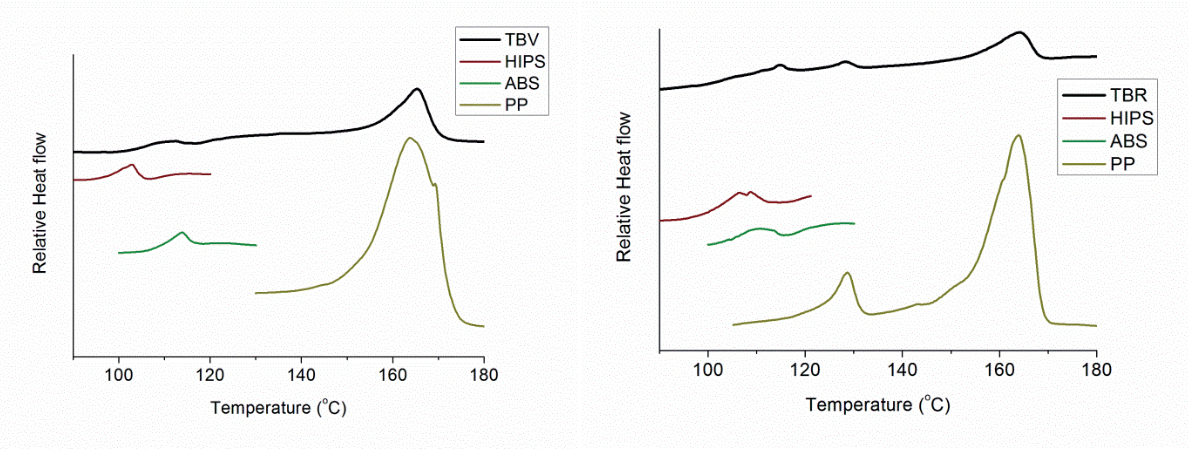

Figure 28: Heat flow curves from DSC showing the transition regions of virgin materials (left) and recycled materials (right). The scales of the curves are the same, but they have been shifted along the y-axis.

6.4. Repeated Recycling of ABS

Relatively few conclusions could be drawn regarding the effects of repeated recycling and accelerated aging on the mechanical properties of pre-irradiated and repeatedly irradiated ABS. No trends could be discerned for σ_y and ε_B. As shown in Figure 29, *E* exhibited a trend-like appearance for the irradiated materials. The non-irradiated reference ABS showed an almost constant *E* with repeated recycling and accelerated aging cycles, as has been reported in similar studies on HIPS [68]. There was a sudden decrease in *E* of both the irradiated ABS materials after the third reprocessing cycle and the second aging cycle. The decrease in *E* contradicted the hypothesis that *E* would increase as a result of cross-linking of the rubber part in ABS, as has been observed elsewhere [90].

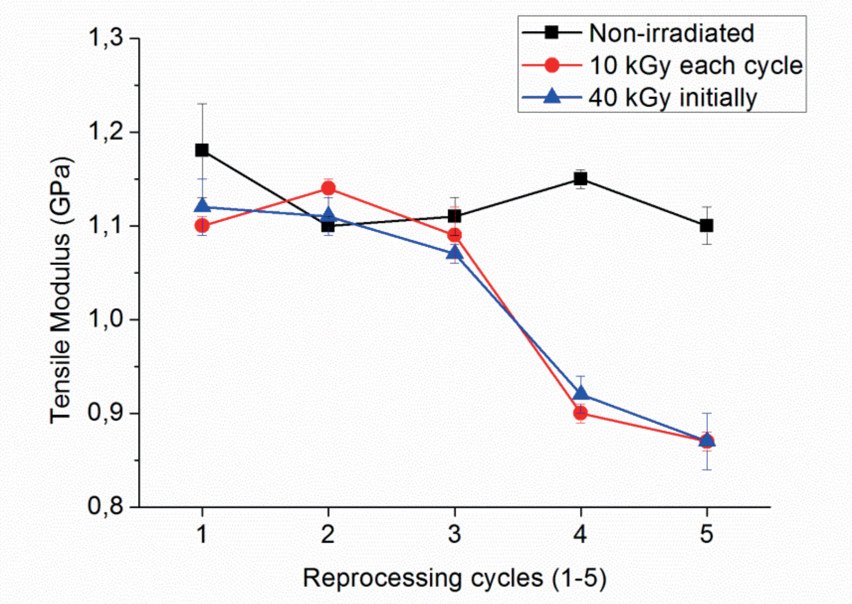

Figure 29: *E* as a function of repeated reprocessing and accelerated aging cycles for ABS that was non-irradiated, irradiated with 10 kGy between each cycle and irradiated with 40 kGy only before the first cycle.

6.5. Rheological Properties of Gamma-Irradiated ABS

The influence of gamma irradiation on WEEE plastic resins is important in order to understand whether radiation could be used to induce reactive compatibilisation in polymer blends. PP has been found to be susceptible to gamma irradiation and to degrade significantly under low doses (0-70 kGy), whereas PS has been found to be very insensitive to gamma irradiation due to relatively high intermolecular forces at temperatures below T_g [91]. ABS, on the other hand, has been less studied in this context and the PB phase in ABS can be expected to be susceptible to gamma irradiation. For this reason, the influence of gamma irradiation on the viscosity of ABS has been studied and is shown in Figure 30 as a function of the corrected shear rate. The viscosity increased slightly with increasing irradiation dose, which indicates that cross-linking occurred, albeit to a small extent. More importantly is however the conclusion that ABS, like PS, appears to be relatively insensitive to the influence of gamma irradiation.

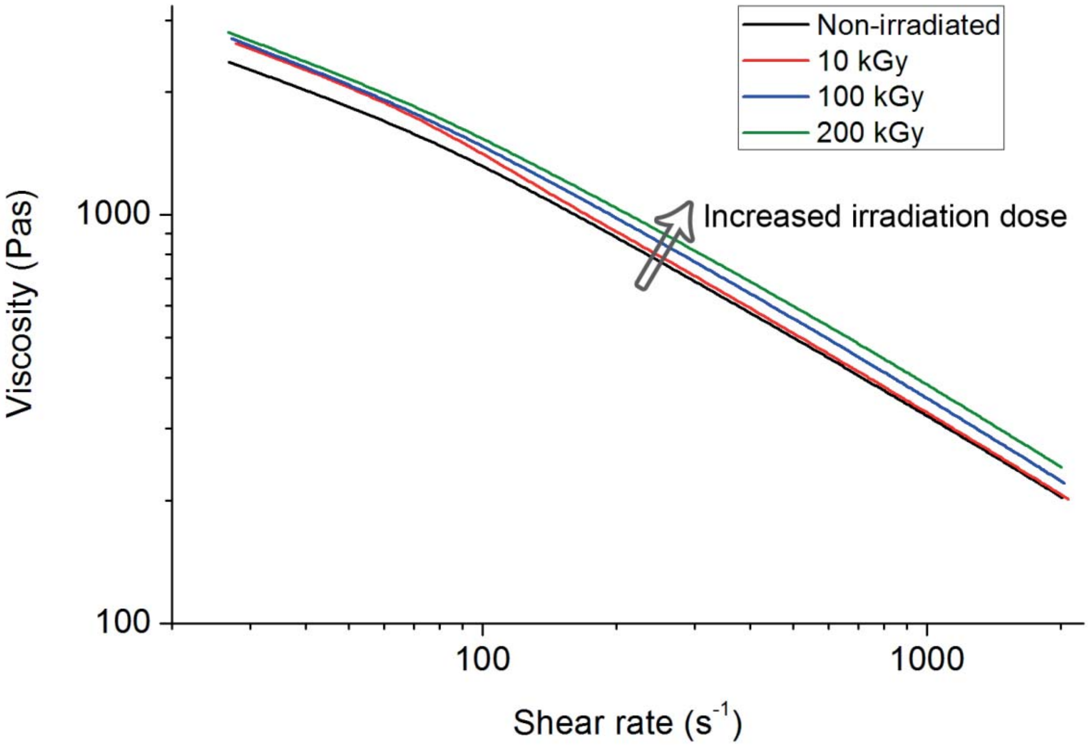

Figure 30: Viscosity as a function of shear rate for ABS that has been irradiated with 0, 10, 100 and 200 kGy.

7. Conclusions

A composition analysis and metal contamination analysis of the WEEE plastics fraction (Stena 1) indicated possibilities for mechanical recycling. Stena 1 was found to contain mainly styrene-based and polyolefin thermoplastics, amounting together to about 95 wt%. Other thermoplastics were found in amounts less than 1 wt %. Non-thermoplastic contaminants were less than 1-2 wt%, mostly wood, rubber and polyurethane foam. Although the non-thermoplastic contaminant level was low, it could reduce the properties of the plastics unless these contaminants are removed prior to mechanical recycling.

Metals that could be classified as hazardous substances were not found in excess of the thresholds levels set by the RoHS directive. Metals such as Fe, Zn and Cu that have a potential to catalyse the degradation of plastics were on the other hand found in significant amounts. Most of these metal compounds could possibly be removed since they were mainly found by surface leaching, and bulk leaching only contributed to significantly higher levels in the case of Mg and Cd.

The composition of the ternary blend model materials (TBV and TBR) of Stena 1 were 47 wt% HIPS, 42 wt% ABS and 11 wt% PP, based on the composition of real waste samples. The joint composition of HIPS and ABS in Stena 1 was found to be relatively stable at 80 ± 4 wt% (calculated with a two-sided 95 % *CI*) with respect to the total composition of the WEEE plastics fraction.

Blending HIPS, ABS and PP without compatibilisation resulted in a lower ε_B of the blend than of any of the single materials, while E, σ_y and ε_y mainly followed the rule of mixtures. Although the low ε_B values and relatively large standard deviations for TBV and TBR indicate incompatibility, this may also be attributed to the low and varying ε_B value of ABS. It appeared to be an almost random event whether ABS was breaking or elongating further, seen as large differences in stress-whitening of similar specimens, which were not seen for HIPS and PP. This can be due to the high yield stress of ABS, which was significantly higher than the stress at break. The recycled materials exhibited higher values of E and σ_y, but lower ε_B than the virgin materials.

Intermediate screw rotation rates (40-80 rpm) and relatively low barrel temperatures (170-220 ^{o}C) were the best processing conditions for achieving reasonably good mechanical properties. Low barrel temperatures were found to be favourable to avoid excessive thermo-oxidative degradation, since T_{ox} of TBV and TBR were found to be 200 ^{o}C and 187 ^{o}C respectively. It was however notable that T_{ox} of TBR was 5-10 ^{o}C higher than would be expected from the rule of mixtures, which indicates that there was no additional thermo-oxidative degradation when recycled ABS, HIPS and PP were mixed. Both blends did however exhibit rather low T_{ox} values with respect to conventional melt-processing temperatures, implying that it might be necessary to increase the amount of active thermo-oxidative stabilisers in order to improve the mechanical performance of the recycled blends.

An intermediate degree of orientation in the extruded specimens was found to improve the mechanical properties. E and σ_y increased almost continuously with increasing degree of orientation, whereas the highest values of ε_B were found for DDR between 4 and 5. Injection moulding also produced oriented specimens, but with a different orientation and with a layered structure having weak adhesion between the layers. The less ductile ABS was possibly migrating to the surface of these specimens.

8. Suggestions for Further Work

The studied model materials of a recyclable WEEE plastics fraction exhibited a relatively low thermo-oxidative stability and low ductility in tension. It would thus be interesting to study different means of improving the character of the blended plastics, possibly by the addition of stabilisers, impact modifiers or physical compatibilisers, or by inducing reactive compatibilisation in the blend.

The plastic blends studied in this work have been model materials. In the further work, melt-blending of real waste material is expected to be important, although it would probably be necessary to remove some of the contaminants, including thermosetting polymers and rubbers. It is also suggested that different melt-processing techniques should be investigated and evaluated with respect to the mechanical and thermal properties of the blends.

9. List of Abbreviations

ABS	Acrylonitrile-butadiene-styrene
BFR	Brominated flame retardant
Br	Bromine
Ca	Capillary number
Ca_{crit}	Critical capillary number
Cd	Cadmium
CI	Confidence interval
Cl	Chloride
DDR	Draw-down ratio
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
E	Modulus of elasticity
E_α	Activation energy
EEE	Electrical and electronic equipment
EPR	Extended producer responsibility
EU	European Union
EVA	Ethylene vinyl acetate
FT-IR	Fourier transform infrared spectroscopy
H_0	Null hypothesis
HBCDD	Hexabromocyclododecane
HIPS	High impact polystyrene
ICP-OES	Inductively coupled plasma optical emission spectroscopy
k	Trend-line slope
MRF	Material recovery facility
OEM	Original equipment manufacturer
OIT	Oxidation induction time
PA	Polyamide
PB	Polybutadiene
PBB	Polybrominated biphenyl
PBDD/F	Polybrominated dioxins and furans
PBDE	Polybrominated diphenyl ether
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PCDD/F	Polychlorinated dioxins and furans
PE	Polyethylene
PET	Poly(ethylene terephthalate)
POM	Polyoxymethylene
POP	Persistent organic pollutant
PP	Polypropylene
PPE (PPO)	Polyphenylene ether
PPE+SB	Polyphenylene ether with styrene butadiene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinylchloride
R	Droplet radii
RoHS	Restriction of the use of certain hazardous substances in EEE
SAN	Styrene-acrylonitrile

Sb	Antimony
SBS	Styrene-butadiene-styrene copolymer
SE	Standard error
SEBS	Styrene-b(ethylene-co-butylene)-b-styrene copolymer
SMMA	Styrene methyl methacrylate
T_g	Glass transition temperature
T_{ox}	Thermo-oxidative degradation temperature
TBBPA	Tetrabromobisphenol A
TBR	Recycled ternary blend
TBV	Virgin ternary blend
UK	United Kingdom
V	Total blend volume
WEEE	Waste Electrical and Electronic Equipment
XPS	X-ray photoelectron spectroscopy

γ	Interfacial tension
δ_A, δ_B	Volume fractions of the polymer resins
ΔG_{mix}	Change in Gibb’s free energy of mixing
ΔH_{mix}	Change in heat of mixing
ΔS_{mix}	Change in entropy of mixing
ε_B	Elongation at break
ε_y	Elongation at yield
σ	Stress
σ_y	Yield stress
φ_A, φ_B	Volume fractions of the polymer resins

10. References

1 Puckett, J., Byster, L., Westervelt, S., Gutierrez, R., Davis, S., Hussain, A.,Dutta, M., *Exporting Harm, The High-Tech Trashing of Asia*, (2002).

2 2012/18/EU, *DIRECTIVE 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on waste electrical and electronic equipment (WEEE)*, L 197 (2012).

3 Robinson, B. H., *E-waste: An assessment of global production and environmental impacts*, Sci. Total Environ., **408,** 183-191 (2009).

4 *WEEE-direktivet i Sverige, En utvärdering med framtidsstudie*, Naturvårdverket, RAPPORT 5969 (2009).

5 Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M.,Böni, H., *Global perspectives on e-waste*, Environmental Impact Assessment Review, **25,** 436-458 (2005).

6 Ongondo, F. O., Williams, I. D.,Cherrett, T. J., *How are WEEE doing? A global review of the management of electrical and electronic wastes*, Waste Manage. (Oxford), **31,** 714-730 (2011).

7 Fischer, C.,Davidsen, C., *Europe as a Recycling Society*, European Topic Centre on Sustainable Consumption and Production, ETC/SCP, 5/2010 (2010).

8 Alston, S. M., Clark, A. D., Arnold, J. C.,Stein, B. K., *Environmental Impact of Pyrolysis of Mixed WEEE Plastics Part 1: Experimental Pyrolysis Data*, Environmental Science & Technology, **45,** 9380-9385 (2011).

9 Martinho, G., Pires, A., Saraiva, L.,Ribeiro, R., *Composition of plastics from waste electrical and electronic equipment (WEEE) by direct sampling*, Waste Manage. (Oxford), (2012).

10 *El-kretsen verksamheten 2011*, El-kretsen,

11 Tojo, N.,Fischer, C., *Europe as a Recycling Society European Recycling Policies in relation to the actual recycling achieved*, European Topic Centre on Sustainable Consumption and Production, ETC/SCP, (2011).

12 Li, J., Lopez N, B. N., Liu, L., Zhao, N., Yu, K.,Zheng, L., *Regional or global WEEE recycling. Where to go?*, Waste Manage. (Oxford),

13 Jalkanen, H., *On the direct recycling of automotive shredder residue and electronic scrap in metallurgical industry*, Acta Metallurgica Slovaca, **12,** 160-166 (2006).

14 Jinglei, Y., Meiting, J.,Williams, E., *Waste electrical and electronic equipment recycling in China: Practices and strategies*, Sustainable Systems and Technology, 2009. ISSST '09. IEEE International Symposium on, (2009).

15 Zoeteman, B. J., Krikke, H.,Venselaar, J., *Handling WEEE waste flows: on the effectiveness of producer responsibility in a globalizing world*, Int J Adv Manuf Technol, **47,** 415-436 (2010).

16 2011/65/EC, *Directive 2011/65/EC of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment*, (2011).

17 Alaee, M., Arias, P., Sjödin, A.,Bergman, Å., *An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release*, Environment International, **29,** 683-689 (2003).

18 Watson, A., Brigden, K., Shinn, M.,Cobbing, M., *Toxic Transformers; - a review of the hazards of brominated & chlorinated substances in electrical and electronic equipment*, Greenpeace Research Laboratories, (2010).

19 Dekant, W., *Risk assessment of TBBPA: Updating the EU Risk Assessment Reports*,

20 Brennan, L. B., Isaac, D. H.,Arnold, J. C., *Recycling of acrylonitrile–butadiene–styrene and high-impact polystyrene from waste computer equipment*, J. Appl. Polym. Sci., **86,** 572-578 (2002).

21 *The 9 New POPs Risk Management Evaluations 2005-2008 (POPRC1-POPRC4)*, Secretariat of the Stockholm Convention, United Nations Environment Programme, International Environment House, Switzerland,

22 Schlummer, M., Gruber, L., Mäurer, A., Wolz, G.,van Eldik, R., *Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management*, Chemosphere, **67,** 1866-1876 (2007).

23 Weber, R.,Kuch, B., *Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated–chlorinated dibenzodioxins and dibenzofurans*, Environment International, **29,** 699-710 (2003).

24 Schlummer, M., Mäurer, A., Leitner, T.,Spruzina, W., *Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE)*, Waste Management & Research, **24,** 573-583 (2006).

25 Rusz Hansen, H.,Pergantis, S. A., *Detection of antimony species in citrus juices and drinking water stored in PET containers*, J. Anal. At. Spectrom., **21,** 731-733 (2006).

26 *Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials*, European Comission, (2010).

27 Tamaddon, F.,Hogland, W., *Review Of Cadmium In Plastic Waste In Sweden*, Waste Management & Research, **11,** 287-295 (1993).

28 Dimitrakakis, E., Janz, A., Bilitewski, B.,Gidarakos, E., *Small WEEE: Determining recyclables and hazardous substances in plastics*, J. Hazard. Mater., **161,** 913-919 (2009).

29 Flaris, V., Singh, G.,Rao, A. R., *Recycling Electronic Waste*, Plast. Eng., **65,** 10-10-15 (2009).

30 Delgado, C., Barruetabeña, L.,Salas, O., *Assessment of the Environmental Advantages and Drawbacks of Existing and Emerging Polymer Recovery Processes*, European Commission, (2007).

31 Freegard, K., Tan, G.,Morton, R., *Develop a process to separate brominated flame retardants from WEEE polymers*, (2006).

32 Wäger, P., Böni, H., Buser, A., Morf, L., Schluep, M.,Streicher, M., *Recycling of Plastics from Waste Electrical and Electronic Equipment (WEEE) – Tentative Results of a Swiss Study*, R'09 World Congress, Davos, Switzerland (2009).

33 Iuga, A., Samuila, A., Neamtu, V., Morar, R., Beleca, R., Das, S.,Dascalescu, L., *Removal of Metallic Particles From Acrylonitrile Butadiene Styrene Wastes Using Electrostatic Separation Methods*, Industry Applications, IEEE Transactions on, **47,** 322-330 (2011).

34 Hainault, T., Smith, D. S., Cauchi, D. J., Thompson, D. A., Fisher, M. M.,Hetzel, C., *Recycling Used Electronics*, (2001).

35 *Recycling and disposal of electronic waste*, The Swedish Environmental Protection Agency, Bromma, March 6417 (2011).

36 Al-Salem, S. M., Lettieri, P.,Baeyens, J., *Recycling and recovery routes of plastic solid waste (PSW): A review*, Waste Manage. (Oxford), **29,** 2625-2643 (2009).

37 Huisman, J., Delgado, C., Magalini, F., Kuehr, R., Maurer, C., Ogilvie, S., Poll, J., Artim, E., Szlezak, J.,Stevels, A., *2008 Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE)*, United Nations University, (2007).

38 Mohabuth, N.,Miles, N., *The recovery of recyclable materials from Waste Electrical and Electronic Equipment (WEEE) by using vertical vibration separation*, Resources, Conservation and Recycling, **45,** 60-69 (2005).

39 Cui, J.,Forssberg, E., *Mechanical recycling of waste electric and electronic equipment: a review*, J. Hazard. Mater., **99,** 243-263 (2003).

40 Freegard, K., Tan, G.,Frisch, S., *WEEE Plastics Separation Technologies*, DEFRA Waste Research Team, (2007).

41 Utracki, L. A., *Polymer Blends Handbook, Volumes 1-2*, Springer - Verlag, (2003).

42 Koning, C., Van Duin, M., Pagnoulle, C.,Jerome, R., *Strategies for compatibilization of polymer blends*, Prog. Polym. Sci., **23,** 707-757 (1998).

43 Vilaplana, F.,Karlsson, S., *Quality Concepts for the Improved Use of Recycled Polymeric Materials: A Review*, Macromolecular Materials and Engineering, **293,** 274-297 (2008).

44 Sperling, L. H., *Introduction to physical polymer science*, 2nd, John Wiley & Sons, (1992).

45 Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A.,Bloch, D. R., *Polymer Handbook (4th Edition)*, John Wiley & Sons, (2005).

46 Shultz, A. R.,Gendron, B. M., *Thermo-optical and differential scanning calorimetric observations of mobility transitions in polystyrene-poly(2,6-dimethyl-1,4-phenylene oxide) blends*, J. Appl. Polym. Sci., **16,** 461-471 (1972).

47 Balart, R., López, J., García, D.,Dolores Salvador, M., *Recycling of ABS and PC from electrical and electronic waste. Effect of miscibility and previous degradation on final performance of industrial blends*, Eur. Polym. J., **41,** 2150-2160 (2005).

48 Lyngaae-Jørgensen, J., Rasmussen, K. L., Chtcherbakova, E. A.,Utracki, L. A., *Flow induced deformation of dual-phase continuity in polymer blends and alloys. Part I*, Polymer Engineering & Science, **39,** 1060-1071 (1999).

49 Perilla, J. E.,Jana, S. C., *Coalescence of immiscible polymer blends in chaotic mixers*, AlChE J., **51,** 2675-2685 (2005).

50 Liu, X., Boldizar, A., Rigdahl, M.,Bertilsson, H., *Mechanical properties and fracture behavior of blends of acrylonitrile–butadiene–styrene copolymer and crystalline engineering plastics*, J. Appl. Polym. Sci., **86,** 2435-2448 (2002).

51 Luo, P.,Wu, G., *Thermo-mechanical degradation-induced grafting of poly(styrene–acrylonitrile) to chlorinated polyethylene*, Polym. Degrad. Stab., **97,** 766-770 (2012).

52 Van Puyvelde, P., Velankar, S.,Moldenaers, P., *Rheology and morphology of compatibilized polymer blends*, Current Opinion in Colloid & Interface Science, **6,** 457-463 (2001).

53 Lindsey, C. R., Barlow, J. W.,Paul, D. R., *Blends from reprocessed coextruded products*, J. Appl. Polym. Sci., **26,** 9-16 (1981).

54 Tarantili, P. A., Mitsakaki, A. N.,Petoussi, M. A., *Processing and properties of engineering plastics recycled from waste electrical and electronic equipment (WEEE)*, Polym. Degrad. Stab., **95,** 405-410 (2010).

55 Elli Lazzaro, I. S., John Bishop, *Recycling of engineering thermoplastics used in consumer electrical and electronic equipment*, Product Lifecycle Management PLM'07, IRIS, Swinburne University of Technology, 533-545 Burwood Rd, Hawthorn, Victoria, Australia (2007).

56 Sani Amril Samsudin, Azman Hassan, Munirah Mokhtar,Jamaluddin, S. M. S., *Effect of SEBS on the Mechanical Properties and Miscibility of Polystyrene Rich Polystyrene/Polypropylene Blends*, Progress in Rubber, Plastics and Recycling Technology, **21,** 261-276 (2005).

57 Campomanes Santana, R. M.,Manrich, S., *Studies on Morphology and Mechanical Properties of PP/HIPS Blends from Postconsumer Plastic Waste*, J. Appl. Polym. Sci., **87,** 747-751 (2003).

58 Gupta, A. K., Jain, A. K., Ratnam, B. K.,Maiti, S. N., *Studies on binary and ternary blends of polypropylene with ABS and LDPE. II. Impact and tensile properties*, J. Appl. Polym. Sci., **39,** 515-530 (1990).

59 Hawkins, W. L., *Thermal and oxidative degradation of polymers*, Polymer Engineering & Science, **4,** 187-192 (1964).

60 Pospíšil, J., Horák, Z., Kruliš, Z., Nešpůrek, S.,Kuroda, S.-i., *Degradation and aging of polymer blends I. Thermomechanical and thermal degradation*, Polym. Degrad. Stab., **65,** 405-414 (1999).

61 Flynn, J. H., *Handbook of Thermal Analysis and Calorimetry*, Elsevier Science B.V., (2002).

62 Brown, M. E.,Gallagher, P. K., *Handbook of Thermal Analysis and Calorimetry - Recent Advances, Techniques and Applications, Volume 5*, Elsevier, (2008).

63 Peterson, J. D., Vyazovkin, S.,Wight, C. A., *Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene)*, Macromol. Chem. Phys., **202,** 775-784 (2001).

64 Santos, A. S. F., Agnelli, J. A. M., Trevisan, D. W.,Manrich, S., *Degradation and stabilization of polyolefins from municipal plastic waste during multiple extrusions under different reprocessing conditions*, Polym. Degrad. Stab., **77,** 441-447 (2002).

65 Murphy, J., *Additives for Plastics Handbook (2nd edition)*, Elsevier, (2001).

66 Dintcheva, N. T., Jilov, N.,La Mantia, F. P., *Recycling of plastics from packaging*, Polym. Degrad. Stab., **57,** 191-203 (1997).

67 Martins, M. H.,De Paoli, M.-A., *Polypropylene compounding with recycled material I. Statistical response surface analysis*, Polym. Degrad. Stab., **71,** 293-298 (2001).

68 Vilaplana, F., Ribes-Greus, A.,Karlsson, S., *Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation*, Polym. Degrad. Stab., **91,** 2163-2170 (2006).

69 Boldizar, A.,Möller, K., *Degradation of ABS during repeated processing and accelerated ageing*, Polym. Degrad. Stab., **81,** 359-366 (2003).

70 Cullis, C. F.,Laver, H. S., *The thermal degradation and oxidation of polybutadiene*, Eur. Polym. J., **14,** 571-573 (1978).

71 Casale, A., Salvatore, O.,Pizzigoni, G., *Measurement of aging effects of ABS polymers*, Polymer Engineering & Science, **15,** 286-293 (1975).

72 Pérez, J. M., Vilas, J. L., Laza, J. M., Arnáiz, S., Mijangos, F., Bilbao, E.,León, L. M., *Effect of Reprocessing and Accelerated Weathering on ABS Properties*, J. Polym. Environ., **18,** 71-78 (2010).

73 Bai, X., Isaac, D. H.,Smith, K., *Reprocessing acrylonitrile–butadiene–styrene plastics: Structure–property relationships*, Polymer Engineering & Science, **47,** 120-130 (2007).

74 Scaffaro, R., Botta, L.,Di Benedetto, G., *Physical properties of virgin-recycled ABS blends: Effect of post-consumer content and of reprocessing cycles*, Eur. Polym. J., **48,** 637-648 (2012).

75 Gerlach, R. W., Dobb, D. E., Raab, G. A.,Nocerino, J. M., *Gy sampling theory in environmental studies. 1. Assessing soil splitting protocols*, J. Chemom., **16,** 321-328 (2002).

76 Hall, W. J.,Williams, P. T., *Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment*, J. Anal. Appl. Pyrolysis, **79,** 375-386 (2007).

77 Morf, L. S., Tremp, J., Gloor, R., Schuppisser, F., Stengele, M.,Taverna, R., *Metals, non-metals and PCB in electrical and electronic waste - Actual levels in Switzerland*, Waste Manage. (Oxford), **27,** 1306-1316 (2007).

78 Hoffmann, P. J., *Linear Regression Analysis: Assumptions and Applications*, Hoffmann, P. John, Department of Sociology, Brigham Young University (2005).

79 Royston, J. P., *An Extension of Shapiro and Wilk's W Test for Normality to Large Samples*, Journal of the Royal Statistical Society. Series C (Applied Statistics), **31,** 115-124 (1982).

80 Montgomery, D. C.,Runger, G. C., *Applied Statistics and Probability for Engineers 4th edition*, 4th edition, John Wiley & Sons, Hoboken, USA (2007).

81 Student, *The Probable Error of a Mean*, Biometrika, **6,** 1-25 (1908).

82 Wilson, D. C., Young, P. J., Hudson, B. C.,Baldwin, G., *Leaching of cadmium from pigmented plastics in a landfill site*, Environmental Science & Technology, **16,** 560-566 (1982).

83 Shawaphun, S., Manangan, T.,Wacharawichanant, S., *Thermo- and Photo-Degradation of LDPE and PP Films Using Metal Oxides as Catalysts*, Trans Tech Publications Ltd, Stafa-Zurich (2010).

84 Yang, R., Christensen, P. A., Egerton, T. A.,White, J. R., *Degradation products formed during UV exposure of polyethylene–ZnO nano-composites*, Polym. Degrad. Stab., **95,** 1533-1541 (2010).

85 Boerrigter, H., Oudhuis, A. B. J.,Tange, L., *BROMINE RECOVERY FROM THE PLASTICS FRACTION OF WASTE OF ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE) WITH STAGED GASIFICATION*, R 2002 Conference, Geneve (2002).

86 Morf, L. S., Tremp, J., Gloor, R., Huber, Y., Stengele, M.,Zennegg, M., *Brominated Flame Retardants in Waste Electrical and Electronic Equipment: Substance Flows in a Recycling Plant*, Environmental Science & Technology, **39,** 8691-8699 (2005).

87 Giles, H. F., Jr., Wagner, J. R., Jr.,Mount, E. M., III, *Extrusion - The Definitive Processing Guide and Handbook*, William Andrew Publishing/Plastics Design Library, (2005).

88 Grancio, M. R., *Cold rolled ABS. Part 1: The effect of rubber particle size on the tensile properties of ABS before and after cold rolling*, Polymer Engineering & Science, **12,** 213-218 (1972).

89 Brachet, P., Høydal, L. T., Hinrichsen, E. L.,Melum, F., *Modification of mechanical properties of recycled polypropylene from post-consumer containers*, Waste Manage. (Oxford), **28,** 2456-2464 (2008).

90 Perraud, S., Vallat, M.-F., David, M.-O.,Kuczynski, J., *Network characteristics of hydrogenated nitrile butadiene rubber networks obtained by radiation crosslinking by electron beam*, Polym. Degrad. Stab., **95,** 1495-1501 (2010).

91 Albano, C., Reyes, J., Ichazo, M., González, J., Hernández, M.,Rodríguez, M., *Mechanical, thermal and morphological behaviour of the polystyrene/polypropylene (80/20) blend, irradiated with γ-rays at low doses (0–70 kGy)*, Polym. Degrad. Stab., **80,** 251-261 (2003).