

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Gamma-irradiation in multi-cycle ABS recycling – effects on ABS properties and  
the recovery of antimony

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover: Injection moulded dog bones from virgin material of ABS, which is a commonly used plastic in electronic equipment. For more information see pages 16, 22 and 29.

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## **ABSTRACT**

Electronic waste, also called waste electrical and electronic equipment (WEEE), is the fastest growing waste stream in Europe today. The fast exchange pace of mobile phones, televisions and computers creates an important need to develop recycling areas to take care of, reuse and recycle these materials. Metals and plastics are equally important to recover from the waste, especially to fulfil the European Directives on the minimum amount of reused and recycled material. In order to facilitate the recycling, this project has looked into the possibilities of leaching antimony (Sb) with various weak acids from one of the main plastic constituents in electrical and electronic equipment (EEE): acrylonitrile butadiene styrene (ABS). Sb is a synergist to brominated flame retardants and a hazardous substance. The influence of gamma-irradiation on ABS has been investigated in a series of experiments. Firstly the hypothesis that irradiation would have a beneficial effect on the recycling of the plastics by re-extrusion, the plastic was also aged by heating it in an oven (90 °C, 144 h). Secondly the effect of irradiation on the rheological properties such as viscosity was investigated. Thirdly, the influence of irradiation on the leaching of the antimony from the plastic was studied. The main results show that antimony can be leached from ABS by heated sodium hydrogen tartrate in dimethyl sulfoxide (DMSO) with an estimated efficiency of 50 %. Gamma-irradiation has an impact on the mechanical and rheological properties of ABS. The yield stress increased with irradiation doses of 0, 10, 50 and 400 kGy. The viscosity also increased in the test samples with irradiation doses of 0, 10, 100 and 200 kGy. In the multi-recycling and accelerated aging test there was a significant reduction in stiffness for the gamma-irradiated samples after the second out of four cycles which is not fully understood. There was no ductile to brittle transition noticed with respect to the strain rate.

Keywords: ABS, WEEE, gamma-irradiation, recycling, antimony, plastics

## List of publications

This thesis is based on the following papers:

- I. **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: Main author, almost all experimental work, data treatment, evaluation and main part of writing the manuscript.

- II. E. Stenvall, **S. Tostar**, A. Boldizar, M. R. StJ. Foreman, Kenneth Möller, *An analysis of the composition and metal contamination of plastics from waste electrical and electronic equipment (WEEE)*. Accepted for publication in Waste Management, 2013.

Contribution: Joint planning and performing of the experiments, in particular the ICP-OES analysis.

- 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: Main author, experimental work, data treatment, evaluation and main part of writing the manuscript.

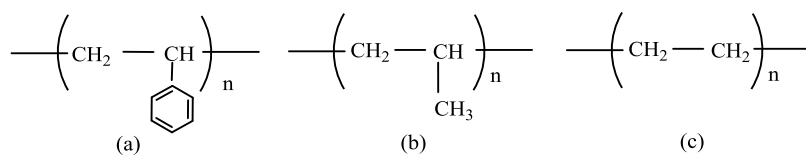
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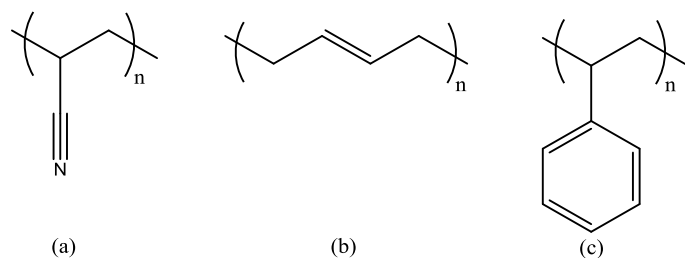
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# 1 Introduction

A polymer is a large molecule built up of many small, identical molecules called monomers, which create a long carbon chain bonded to other elements [1, 2]. The chains can be linear, branched or crosslinked. Plastics are one or more polymers together with additives and are normally produced from fossil oil or natural gas [1]. Plastics are divided into two groups: thermoplastics and thermosets. The thermoplastics can be melted and reformed into new object while the chemical structure in thermosets is so well crosslinked and cannot be released upon heating. The thermosets will thus then decompose instead of melt when reheated. They can though be used as fillers in new products since thermosets can be pulverized into powder [1, 3, 4]. The word plastic comes from the Latin word *plasticus*, which means ‘mouldable’, or the Greek word *plastikos*, which means ‘to mould’ [5]. The development of plastics escalated during the 19<sup>th</sup> century. It started off in the 1820s with vulcanized rubber [1]. Cellulose nitrate was the first artificial plastic, showed at the International Exhibition in London in 1862 [3]. It became popular and was used in a wide range of products including combs and babies’ rattles. In 1872, the Hyatt brothers patented the first injection moulding machine to manufacture plastic objects in line. If the 19<sup>th</sup> century focused on natural polymers, the 20<sup>th</sup> century focused on synthetics such as Bakelite, urea-derived polymers and nylon. In 1935, the first extruder was produced for thermoplastics by Troester in Germany [6], and Carothers together with DuPont patented nylon [7]. In 1937, IG Farben in Germany started the first commercial production of polystyrene (PS), and in 1939 Imperial Chemical Industries (ICI) in the United Kingdom produced the first commercial polyethylene (PE) [6].



**Figure 1.1.** The repeating units for (a) PS, (b) PP and (c) PE.



**Figure 1.2.** The three monomers in ABS: (a) acrylonitrile (the A - part in ABS), (b) 1, 3 butadiene (the B - part in ABS) and styrene (the S - part in ABS).

During the Second World War, plastics came to play a big role in technical equipment, e.g. PE in radar. Polyacrylonitrile (PAN), polyethylene terephthalate (PET) and the first polyester fibre, Terylene®, together with ‘superglue’ (methyl cyanoacrylate), ABS, high-impact polystyrene (HIPS) and Lycra®, were all invented during the 1940s [6]. In the 1950s, the focus shifted slightly and it was all about fashion (fabrics) and home decoration. ABS copolymer, PS foam and the PE bag were developed. Lego was patented in 1958, and toys were produced in cellulose acetate, which was later changed to ABS [6]. During the 1960s and 1970s, the focus was still on colour and design, though Kevlar® was invented by DuPont in 1965 and PET bottles were manufactured in 1973. In 1976, plastic became the most used material in the world [6]. During the 1980s and 1990s, the focus changed to high-performance materials. In 1980, the first linear low-density polyethylene (LLDPE) was produced. In 1982, the first artificial heart, mostly made of polyurethane (PU), was implanted in a human [6]. The 2000s were the age of nanotechnology. The National Aeronautics and Space Administration (NASA) decided that the polyethylene-based material RFX1 would be the material used in the spaceships going to Mars in the future. Boeing 787, ‘Boeing’s plastic dream’, was manufactured in 2009. The skin was made of up to 100 % plastic composites with a total of 50 % plastic in the whole aircraft. [6].

The light and flexible plastic material has become a substitute for steel and other materials in many applications in, for instance, the automotive and medical industry. The amount of plastic in cars has now increased to 12 % of the total weight. There are different sorting processes in the car industry, one of which is the Galloo process in which four different types of plastic are separated and the materials recycled: polypropylene (PP), ABS, PE and PS [8].

It is easy to add additives to enhance certain desired properties of plastic, allowing it to be used in many different applications [4].



The use of plastics has increased dramatically since the 1950s, especially in the electronic sector where the development of new electronic products has escalated and there is a fast exchange rate of computers and mobile phones [1, 9]. The recycling of plastics has become more important to prevent the accumulation of waste from it. Legal demands and directives are also striving towards higher recycling levels for the producers of the products, which require new techniques and concepts from the recycling companies to be able to handle the plastics, particularly from WEEE. It is particularly important to increase mechanical recycling of the thermoplastic material instead of land filling them, or burn them for energy recovery, which still is a common disposal method in the world [10].

The energy savings of recycling plastics instead of using virgin materials are enormous: 80 % of the energy and 1-3 tons of CO<sub>2</sub> are saved for every ton of virgin plastic that is replaced [11].

Nevertheless, there are some difficulties with plastic recycling compared with, e.g., metal recycling. In principle, plastics can have any colour, and the density span is very narrow making plastics hard to separate by density, especially for light materials. PE, for instance, can contain additives that give it the same density as a heavier plastic such as ABS [11, 12].

## **1.1 Objective**

In this project, the objective is to better understand what recycled WEEE plastics can be used for, by making a plastic blend of mixed electronic waste miscible and enhancing the mechanical properties of the recycled material. One benefit of using a plastic blend is that it requires less pre-treatment, such as the sorting steps for recycled materials. Studies of the processing and properties of separated plastics can help in understanding how the plastic blend will behave and will be answered in this thesis. The compatibility of mixed plastics can be improved by additives and/or reactive processing.

The work is not industry initiated, but close collaboration has been set up together with different recycling companies in Sweden such as Stena Metall AB, SIMS recycling and Renova.



## 2 Background

### 2.1 WEEE in general

Waste electrical and electronic equipment (WEEE) is a generic term for electronic equipment such as mobile phones, computers, household equipment and other products, some of which may not be expected, such as toys. It can simply be described as every product that contains a battery or an electrical cord. Light bulbs and batteries are also included in the WEEE category. Today, the WEEE fraction is approximately 5 % of all municipal solid waste (MSW) [13]. WEEE is the fastest growing waste stream in the EU15 states<sup>1</sup> with a growth rate almost three times higher than the average MSW [13-15]. Some 20-50 million tons of electronic waste are generated worldwide annually, but only 10 % is handled correctly in recycling facilities. A large amount ends up in the normal MSW stream or is exported to China or Africa for manual dismantling to recover the precious metals [13]. In Europe, 10 million tons of WEEE is generated every year. This figure is estimated to increase to 12.3 million tons by 2020 [16, 17].

WEEE is regulated in Directive 2002/96/EC, which came into effect on August 12, 2005 and was updated in 2012 to Directive 2012/19/EU. The aim was to get less material to end up in landfill sites, to reduce the exportation of waste and to make use of valuable secondary raw material [18]. The directive on the Restriction of use of certain Hazardous Substances in electrical and electronic equipment (RoHS) regulates that lead (Pb), mercury (Hg), cadmium (Cd), chromium (VI) (Cr<sup>6+</sup>), polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) are not allowed in electronic equipment [19].

Electronic goods (including batteries) are regulated by the extended producer responsibility (in total there are seven different categories, e.g. packages/newspapers and tires), meaning that the manufacturers are responsible for the collection and recycling of the electronic waste. The products have an extra fee to finance this [20]. In Sweden, this is handled by an organization called El-kretsen, which was founded by the industry in 2001, to help producers meet their obligations. El-kretsen has nationwide coverage for collection and recycling systems for households and industries through collaboration with the municipalities.

<sup>1</sup> The EU15 states: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden and the United Kingdom

material or energy. The producers collected 161 439 tons of electronic waste in 2010, which is 17.2 kg per person. This number is very high compared with the target set by the WEEE Directive of collecting 4 kg per person which some other EU countries have difficulties to reach [21].

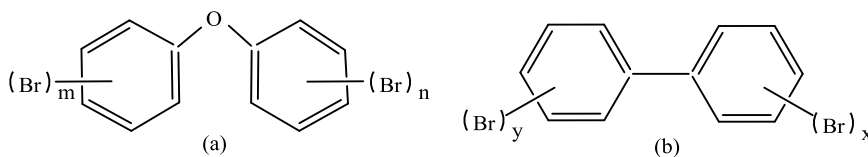
According to the EU directive on WEEE, electronic waste is classified in ten different categories; see Table 2.1.

**Table 2.1.** WEEE categories according to the EU directive on WEEE [18, 22].

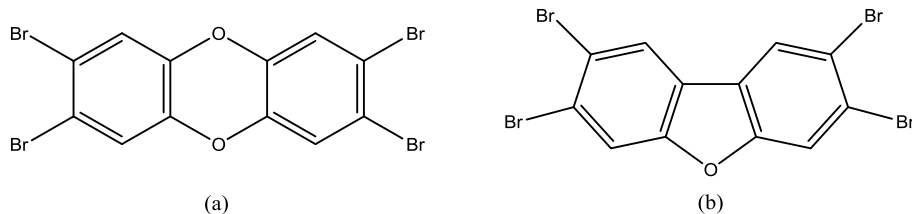
No	Class of item	Label	Recycling goals (weight %)	
			Material recycling	Material recycling incl. energy recovery
1	Large household appliances	Large HH	75	80
2	Small household appliances	Small HH	50	70
3	IT and telecommunications equipment	ICT	65	75
4	Consumer equipment	CE	65	75
5	Lighting equipment	Lighting	50	70
6	Electrical and electronic tools (with the exception of large- scale stationary industrial tools	E & E tools	50	70
7	Toys, leisure and sports equipment	Toys	50	70
8	Medical devices (with the exception of all implanted and infected products)	Medical equipment	None	None
9	Monitoring and control instruments	M & C	50	70
10	Automatic dispensers	Dispensers	75	80

## 2.2 WEEE plastics recycling – what can and cannot be recycled?

Metals have been recycled for a long time due to their value and the dwindling mineral reserves that are economical to mine. Plastics on the other hand have been seen more as a by-product. Electronic waste has mostly been incinerated, and thus energy recovered, due to the fact that the plastics used in WEEE often contain flame retardants (FRs). The flame retardants may be bromine based and some, the PBDE and PBB, shown in Figure 2.1, are regulated by the RoHS directive, which states that they are now prohibited for use in new products (the limit for PBDE and PBB in products are 0.1 %) and the material is not allowed to be recycled due to its potential of forming dioxins/furans [19].



**Figure 2.1.** Molecular formulas of (a) PBDE and (b) PBB.



**Figure 2.2.** An example of a dioxin: 2, 3, 7, 8-tetrabromodibenzo-*p*-dioxin (TBDD) and a furan: 2, 3, 7, 8-tetrabromodibenzofuran (TBDF).

However, these types of flame retardants are allowed to be used in other parts of the world, which means that they can still occur in plastic products. Existing products containing these restricted flame retardants are still in use within Sweden, and enters the Swedish waste streams in a slow pace.

As well as the problems of hazardous substances in plastics recycling, obstacles include degradation and immiscibility of the plastics. Due to the mechanical treatment and heating of plastics, the polymer bonds or chains are shorter and the plastics degrade. Additives such as stabilizers are often added to the plastics to make them more resistant to this issue [4]. The third problem is due to the heterogeneity of different plastics types, which results in poor phase adhesion and properties when blended. To overcome the heterogeneity issue, different types of

compatibilizers can be used, such as reactive compatibilizers (in situ formation of block and grafted copolymers) [23], physical compatibilizers (adding pre-made block or graft polymers) and interpenetration networks [24, 25]. The compatibilizer serves three purposes: to align the interfacial tension and obtain the wanted dispersion, to make sure that the morphology made during the blending gives the optimum structure during the forming stage and to increase the adhesion between the phases in the solid state [25].

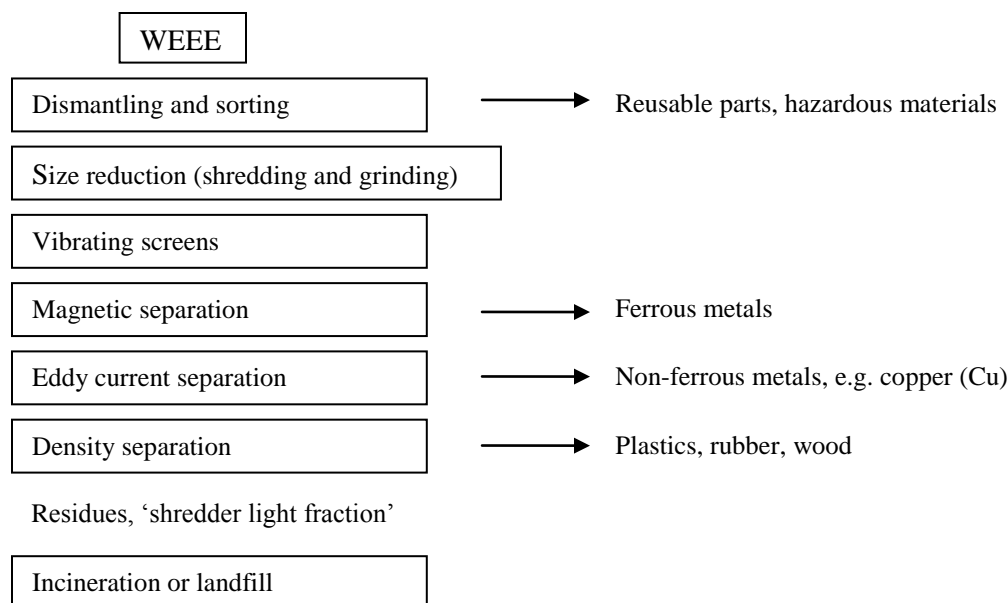
### 2.3 WEEE plastics composition and separation

The WEEE plastics segment contains more than 15 different engineering plastic types [26]. To work with recycled plastics, it is therefore important to know the composition of the incoming plastics to the recycling facilities. WEEE plastics often contain contaminants such as rubber, metal, paper, wood, gravel, glass, wires and moisture [13]. These contaminants have to be removed before the plastics can be recycled.

The plastics and contaminants separation can be managed by different sorting systems such as density bath separation, magnetic separation, cyclone separation, mid-infrared (MIR) or X-ray scanning [13, 27].

#### 2.3.1 Recycling of WEEE plastics under controlled conditions

To show the plastics recycling journey, the whole WEEE loop must be included. A typical setup for taking care of WEEE can be seen in Figure 2.3.



**Figure 2.3.** Schematic picture of a typical WEEE recycling process [13].

The recycling process starts with manual dismantling and sorting of the components that can be reused, and valuable parts like metal and glass are removed and treated. Hazardous substances, e.g. components containing mercury, batteries, cathode ray tube (CRT) glass and liquid crystal displays (LCDs), are taken out for further treatment [12]. The remaining parts are then shredded or grinded and sorted in different steps according to their different physical properties: density, shape, weight, electrical and magnetic properties. The sorting techniques are density or gravity separation (water or airflow tables, sifting, heavy media floating) for plastics, eddy current separation (electric conductivity) for non-ferrous metals and magnetic separation for ferrous parts [13]. Further treatment can be performed on the plastics stream with X-rays, e.g. X-ray fluorescence (XRF), to determine if the plastics contain BFR [28], or infrared (IR) treatment, e.g. MIR, to distinguish between and sort different plastic types and colours [29]. When this is done, new additives (e.g. thermal stabilizers or colorants) may need to be blended with the recycled plastics to obtain the same or similar properties as those of virgin plastics.

### **2.3.2 Recycling of WEEE plastics under uncontrolled conditions**

In the developing countries, it has become common to recycle WEEE with very basic tools in small workshops in an uncontrolled manner. The aim is to recover all the valuable materials, such as plastics, copper, aluminium (Al) and steel. The initial recycling steps are performed manually with bare hands, hammers and screwdrivers. After dismantling, the metals can be extracted by acids and the plastics further shredded and separated by density or colour. A simple test used for determining the plastic type is to heat a piece of plastic and then blow out the flame and smell the plastic gasses. This can result in exposure to toxic fumes and is not recommended. The plastics are then melted and extruded in order to be used in new objects. Plastics with non-matching colours or impurities are piled or burnt on open fires releasing toxic and volatile substances into the air. The residues are dumped in open fields and toxic substances are leached into the soil and groundwater and/or nearby surface waters [13, 30].





## 3 Theory

### 3.1 Gamma-irradiation

Gamma-irradiation has been used for a long time as a sterilizing method for the food- and packaging industry and in hospitals. It is electromagnetic ionizing radiation of the same kind as light or radio waves but with much higher energy that comes from radioactive decay. For the irradiation a  $^{60}\text{Co}$  source was used. Two characteristic gammas at 1172 keV and 1332 keV are emitted promptly from the  $^{60}\text{Ni}$  (nickel) formed by the beta decay of  $^{60}\text{Co}$  according to equation 3.1 [31].



$\beta$  particles are high energy electrons or positrons emitted by different types of radioactive decay. The particles can travel circa 10 meters in air and are stopped by an aluminium sheet.

$\bar{\nu}$  is the antiparticle to the neutrino with almost no mass, it has no charge and are created due to certain types of nuclear reactions or radioactive decays. The neutrinos are not affected by electromagnetic forces and can therefore pass through matter unimpeded [31].

### 3.2 The influence of gamma-irradiation on polymers

Gamma rays are known to influence plastics either through chain scissoring (degradation or decrease in molecular weight) or crosslinking (increase in molecular weight) of the polymer chains due to the formation of free radicals; see Table 3.1 [32]. This behaviour is dependent on the plastic type and causes changes in the mechanical properties of the plastics. The aim of using gamma-irradiation in this work is to enhance the mechanical properties of the plastics in order to recycle them into similar or almost as good products as before recycling [33]. Polymer mixtures are generally also immiscible and incompatible, leading to poor phase adhesion and properties when blended. Another purpose of the gamma-irradiation is therefore to see if free radicals can allow them to graft on monomers such as acrylates or methacrylates, making new side chains, which can make the immiscible polymers compatible [34].

**Table 3.1.** Effect of radiation on polymers.

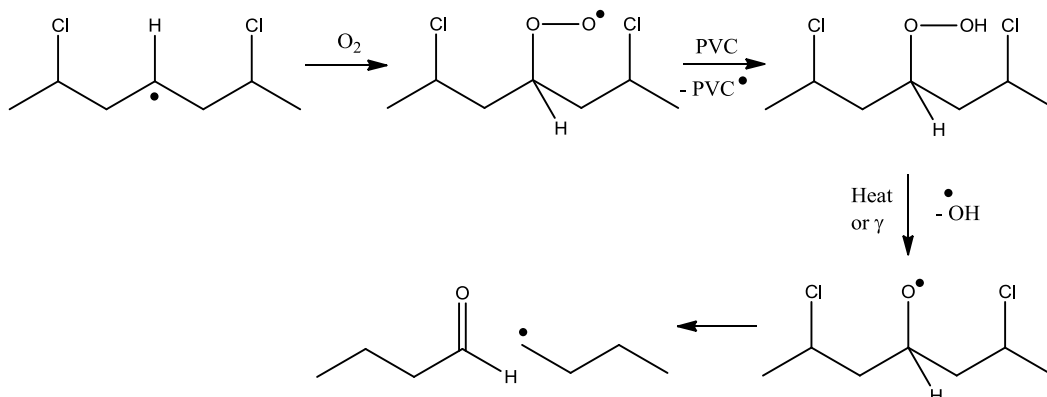
Predominant crosslinking	Predominant degradation
Polyethylene	Poly(isobutylene)
Polypropylene	
Poly(vinyl chloride)	Poly(vinylidene chloride)
Poly(acrylonitrile)	Poly( $\alpha$ -methacrylonitrile)
Poly(acrylic acid)	Poly(methacrylic acid)
Poly(acrylates)	Poly(methacrylates)
Polystyrene	Poly( $\alpha$ -methyl styrene)
Natural rubber	
Synthetic rubber (except poly(isobutylene))	
Polyamides	Poly(ethylene terephthalate)
Poly(ethylene oxide)	Cellulose plastics

**3.2.1 Radiation effect on long-chain polymers**

When long-chained polymers are irradiated, one single change in one bond per molecule, in a polymer with a molecular weight of approximately  $10^6$ , can change the physical properties hugely. Thus, only a modest irradiation dose is necessary to create an effect on the polymer chain [33].

**3.2.2 Chain scission in linear polymers**

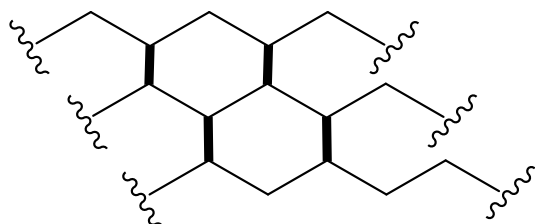
Oxygen is well known to react with many free radicals, for example the oxygen inhibits the radical polymerisation of styrene. If oxygen is able to react with the polymer radicals then they will not persist sufficiently long for them to get together. Instead the polymer radicals are intercepted by the oxygen to form stable peroxy radicals, which abstract a hydrogen from another polymer chain to form an alkyl hydroperoxy. Thermolysis of an alkyl hydroperoxy forms an oxygen centred radical which has a high energy. These often undergo beta scission reaction thus fragmenting the molecule. A low dose rate allows more time for the oxygen to diffuse into the plastic so the plastic will remain oxygenated to a greater depth. While at higher dose rates the interior of the plastics become more deoxygenated because the oxygen is not able to diffuse sufficiently quickly into the plastic to replace the oxygen consumed by reaction with radicals.



**Figure 3.1.** Formation of peroxy radicals and the chain scissoring of a polymer, in this case a PVC.

### 3.2.3 Crosslinking

Polymer molecules can be linked together in various ways, with random crosslinking being the most studied behaviour. There are different types of links, such as: 1) linking of two molecules by a short link or 2) series of short bonds (randomly distributed), 3) end linking, 4) internal linking, 5) enhanced crosslinking, 6) entanglements, which are more temporary, and 7) hydrogen (H) bonding [33].



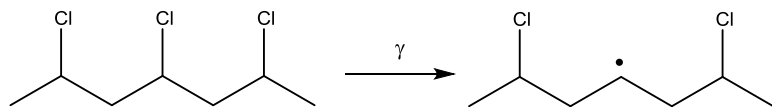
**Figure 3.2.** Crosslinked polymer.

The important process when crosslinking appears is the change in molecular weight, which can lead to huge changes in the physical properties. The behaviour is different for low dose and high dose radiation crosslinking. For small radiation-induced crosslinking, the number of intermolecular crosslinks is proportional to the dose over a very large range. The crosslinks are also randomly distributed. However, the random distribution is not valid for all plastics, e.g. PE, since it is partly crystalline at room temperature. When the average molecular weight is increased by crosslink density, it is more likely to take part in another crosslink, since the molecule

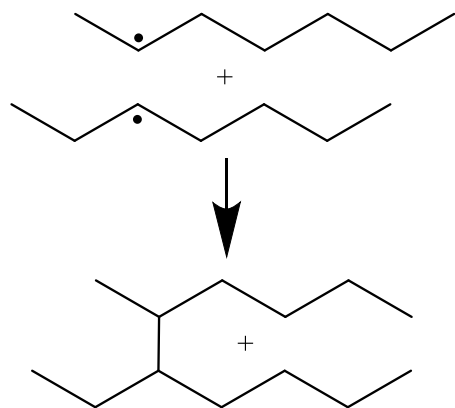
becomes larger. For every crosslink made, the number of separate molecules is reduced by one [33].

When crosslinking increases due to higher irradiation doses, chances are that there will be crosslinks within the same molecule and the chances of involving an independent molecule are less. The branching of the internal molecules involved will increase and cause a partly closed loop. This is difficult to show with simple viscosity relations. There is a phenomenon called gel point, which occurs when the crosslink density exceeds a critical value, that gives an insoluble and non-converging, three-dimensional network formed between individual molecules [33].

Anaerobic radiolysis mechanisms (crosslinking) of PVC can be seen in Figure 3.3. The crosslinking mechanism is similar for other plastics as well [35].



**Figure 3.3.** Formation of alkyl radicals.

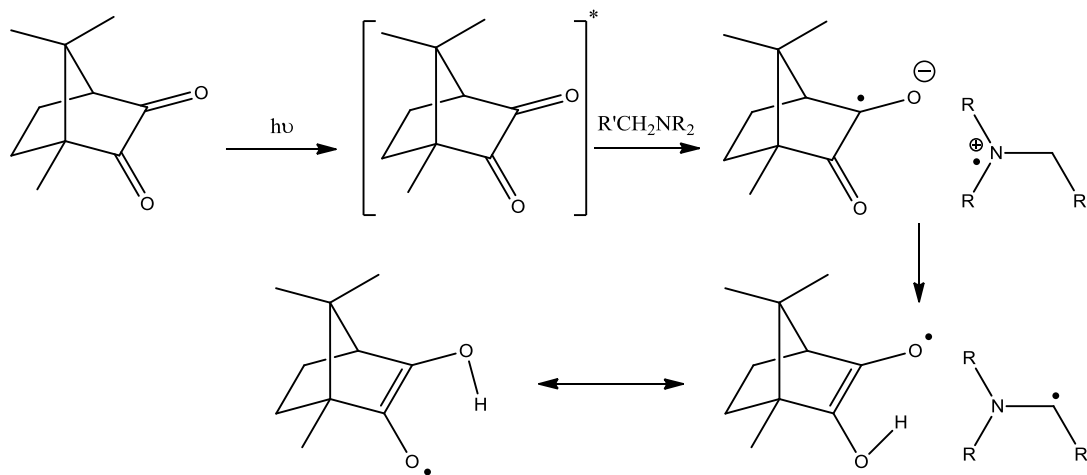


**Figure 3.4.** Crosslinking reactions.

### 3.3 Photopolymerization

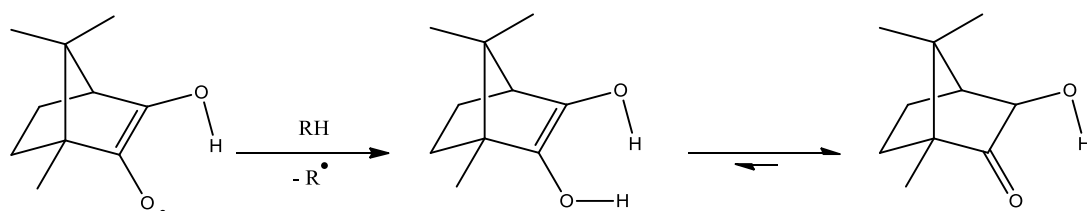
Photopolymerization is another method to get a crosslinked network by a radical reaction and is used in dental applications for instance. The radicals required to start the chain reaction are formed by photochemistry. The pi ( $\pi$ ) system of a diketone absorbs light and thus entering an excited state. The diketone then reacts (intermolecular hydrogen abstraction) with a tertiary amine by electron transfer. The nitrogen centred radical formed from the amine then rearranges

into a  $\alpha$ -heteroatom stabilised radical which then reacts with the monomer, thus starting the chain reaction [36].



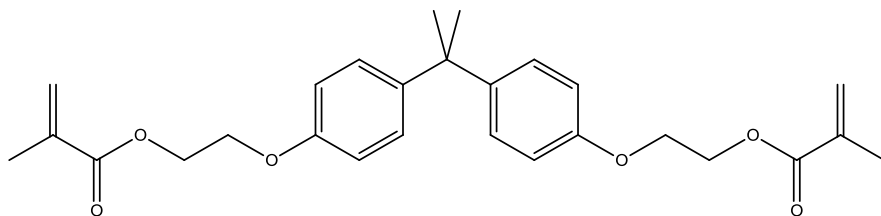
**Figure 3.5.** The photochemical intermolecular hydrogen abstraction of a diketone (Camphorquinone) with an amine.

The radical is formed by reduction of the diketone may react with a hydrogen atom donor (by an intermolecular hydrogen abstraction) to form a dihydroxyalkene which tautomerises into a hydroxyketone.



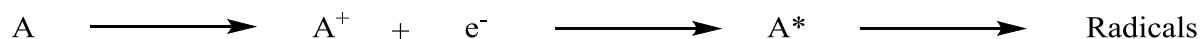
**Figure 3.6.** The second intermolecular hydrogen abstraction by the reduced diketone.

A typical dimonomer used in dental applications is ((propane-2,2-diyl-*bis*(4,1-phenylene))*bis*(oxy))*bis*(ethane-2,1-diyl) *bis*(2-methylacrylate) which is formed from bisphenol-A is shown in Figure 3.7. This compound has two alkenes which are conjugated to carbonyl groups and are thus very able to undergo a radical polymerisation reaction [37].



**Figure 3.7.** The dimonomer used in dental applications ((propane-2,2-diyl-*bis*(4,1-phenylene))*bis*(oxy))*bis*(ethane-2,1-diyl) *bis*(2-methylacrylate).

This formation of radicals by electron transfer followed by a hydrogen transfer is very similar to the formation of radicals when organic matter is irradiated with ionising radiation, which is described in Figure 3.8 [31].



**Figure 3.8.** Radicals formation in organic matter by recombination of the electron with the geminate (e.g. original ion pair) radical cation.

### 3.4 Antimony

Antimony, atom number 51, is a shiny, silvery, brittle and semiconducting semi-metal with the Latin name stibium [38, 39]. It is found in sandstone and volcanic rocks at an average content of  $1 \text{ g ton}^{-1}$ . There are three possible oxidation states for natural antimony: the metallic or covalent (0) state, and the (III) and (V) states [38]. As pure antimony has poor mechanical properties, it is used in small quantities, yet, larger amounts are used for alloys and in compounds. Antimony is a by-product of different mines: gold (Au), silver (Ag), lead and zinc (Zn), with the world's resources located in Bolivia, China, Mexico, Russia and South Africa [39]. Antimony is used as a catalyst in 90 % of all PET production, as an opacifier [40] in the glass industry, in lead batteries, in zinc and lead alloys to increase hardness [39], and as white pigment in paint [41]. The most important field of use for antimony, however, in the form of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ), is as a synergist to BFR [39]. The  $\text{Sb}_2\text{O}_3$  itself does not have flame retardant properties but acts as a catalyst, helping the halogenated flame retardant to break down into active molecules. It can also react with the flame retardant to form volatile antimony halide compounds, giving the same effect as the halogenated flame retardant of removing the high energy radicals that feed the fire [42].  $\text{Sb}_2\text{O}_3$  is produced by roasting stibnite ores, as a vapour-phase reaction at high temperatures above  $1500 \text{ }^\circ\text{C}$ , which can contain 55 % antimony [43]. Antimony trioxide is suspected to be a

carcinogen and is listed as a priority pollutant by the United States Environmental Protection Agency (EPA), the European Union (EU) and the German Research Foundation (DFG) [40, 44]. The reason it may be of interest to recycle antimony is that it has been included on the EU's list of critical raw materials [45] as being at risk of a supply shortage, making antimony economically valuable.





## **4 Materials and methods**

### **4.1 Materials**

For the sodium hydrogen tartrate in the DMSO solution test, a discarded computer housing made of ABS, of a flame retardant grade, manufactured in China in January year 2000, was used. Test samples were cut into 2 x 2 cm pieces.

In the degradation study of ABS, using repeated processing and accelerated aging, a high flow grade of ABS for injection moulding from BASF was used: Terluran GP35 without flame retardants, purchased at Albis.

For the WEEE plastics composition study, three different batches were investigated. The first, a batch of 600 kg of material, was collected at Stena Technoworld in Halmstad on 05/07/2011, henceforth called Stena 1. This low-density fraction contains material from different types of mainly styrene-based (80 %) electronic waste, from commercial enterprises and private consumers. It has a very low content of brominated flame retardants (BFR), which is checked by Stena Technoworld at regular intervals. The second batch from Stena Technoworld, henceforth called Stena 2, was collected at the same site on 12/01/2011. The Stena 2 batch did not contain plastics from large white goods, like refrigerators, washing machines and stoves. The two batches from Stena Technoworld had been sorted out from metals, ceramics and high-density plastics. The third and last batch, henceforth called Sims, was collected from Sims recycling in Katrineholm on 23/05/2011. The flake size was bigger in this batch compared with that in the batches from Stena Technoworld. The batch also contained plastics with and without BFR additives and small fractions of glass, ceramics, composites and non-ferrous metals.

### **4.2 Methods**

#### **4.2.1 ICP-OES**

Inductively Coupled Plasma – Optical Emission Spectroscopy is a test method to analyse the concentrations of different elements in a solution. The liquid solution is atomized in the plasma, which has a temperature of 6000-7000 K, giving the atoms high excitation energy and thus causing them to emit electromagnetic radiation that is detected by the optical emission detector. The model used was a Thermo iCAP 6500 equipped with an autosampler and iTEVA software. For further information about ICP – OES, see the information given by Dean [46].

#### **4.2.2 FTIR-ATR**

Fourier transform infrared spectroscopy – attenuated total reflectance is used to see the functional groups in the polymer and was performed using a Thermo Electron Corporation Nicolet 6700 fitted with a DurasamplIR II. The spectra were recorded by means of an attenuated total reflectance attachment using a diamond crystal and OMNIC software. The treated samples of plastic were washed three times with distilled water before the measurement to remove any remaining leaching media. The spectra were corrected with respect to water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>).

#### **4.2.3 Capillary rheometer**

A capillary rheometer was used to determine the viscosity of the material, which indicates changes in molecular weight distribution, crosslinking or chain scission. The Göttfert rheograph 2002 together with the software WinRHEO was used at ten different shear rates from 20-1500 s<sup>-1</sup>. The first two measurements in each test were excluded due to unstable values. Triplicates were performed at three different capillary lengths: 10, 20 and 30 mm, all with 1 mm diameter. The temperature was kept at 190 °C for all tests. The test results were corrected according to both the Bagley- and Rabinowitsch corrections.

#### **4.2.4 Elemental analysis**

Elemental analysis is a test method used to give a quantification of the concentrations of different elements in a material. The amounts of carbon (C), hydrogen (H), nitrogen (N), bromine and antimony were determined in the ABS plastic. The CHN analysis was carried out using a Carlo Erba 1112 elemental analyser. The Br was carried out by oxygen flask combustion followed by titration. The Sb analysis was carried out by acid digestion followed by analysis using a Varian Vista MPX ICP – OES. The test was performed by Medac LTD in England.

#### **4.2.5 SEM-EDS**

Scanning electron microscopy – energy dispersive spectroscopy is an elemental analysis method. A microscope is equipped with an electron beam that scans the surface of the specimen, and the elements can be determined due to differences in the atomic structures, giving each element a specific pattern of peaks in an X-ray spectrum [47].

#### **4.2.6 Gamma-irradiation source**

The gamma-irradiation was performed in a Gammacell 220 (Atomic Energy of Canada, now called Norion). The dose rate to water in the irradiation chamber of this unit was 14 kGy hr<sup>-1</sup> on average. It was a little lower at the edges of the chamber (13 kGy hr<sup>-1</sup>) and higher in the centre (15 kGy hr<sup>-1</sup>), and the dose rate was measured with the ferrous-cupric sulfate dosimeter test (19/04/2012) [48]. The temperature within the chamber is approximately 50 °C.



## 5 Experimental

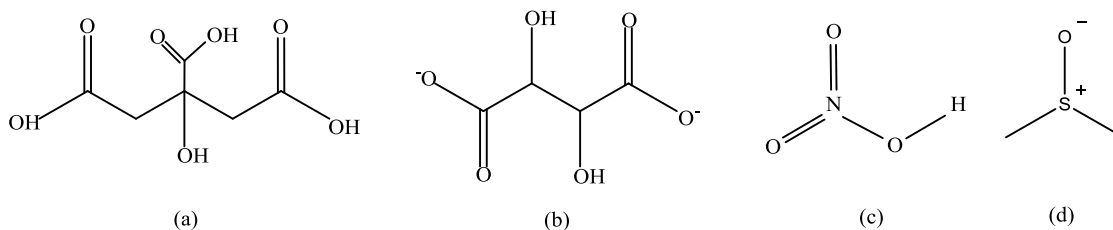
### 5.1 Composition analysis of mixed WEEE plastics

Fourteen samples from Stena 1 were taken in succession from a falling plastics stream from a density bath within a period of 3 hours. Each sample weighed between 90 and 210 g and contained on average 90 flakes. A total of 1226 flakes were analysed from the Stena 1 batch. Three samples were taken from a falling stream at the Sims recycling, weighing 370-460 g each and 340 flakes were analysed from this batch. Three samples, each weighing 110-120 g, came from Stena 2 batch. They were collected by the coning and quartering sample splitting method [49], and 230 flakes were analysed from the Stena 2 batch. All the samples were washed three times with water and then dried in an oven for 1 hour at 50 °C before they were analysed with FTIR.

The characterization was achieved by individual peak interpretation and comparison of the spectra with those from known samples and with spectra stored in databases as well as in IR spectrum atlases.

### 5.2 Leaching of antimony with citric and tartrate acid and/or DMSO

Weak acids such as citric acid and tartrate acid were evaluated in a pre-test on fly ash to see the leaching ability of antimony.



**Figure 5.1.** Molecular formulas for (a) citric acid, (b) tartrate acid, (c) nitric acid and (d) DMSO.

The reason for choosing these acids was that the influence of the acids should be as small as possible on the plastic itself. Previous results by Shotytk et al and Bach et al show that antimony migrates from PET bottles into the bottled water or citrus juice [44, 50]. The hypothesis was that citric acid could have enough effect on the antimony leaching out of the ABS plastic. An initial leaching test (about 24 hours) was performed on fly ash from municipal solid waste burned (1000-1100 °C) in a grate-fired boiler in Linköping. Sodium hydrogen tartrate (0.5 M, room

temperature and heated to 100 °C) and citric acid (0.5 M, room temperature) were used. The ash to acid ratio was 1:6, 1:9 and 1:8. The results from the ash leaching determined the leaching acids for the computer plastic.

The ABS pieces from the computer housing were leached in sodium hydrogen tartrate (0.5 M) (room temperature and heated to between 100-108 °C) and dissolved in either DMSO or water. Pure DMSO (heated) and water (room temperature) were used on their own as leaching media in a control experiment. The samples were heated (20 hours) in glass containers connected to Liebig condensers to re-circulate the vapour. The DMSO samples were cooled (50 hours) and most of the re-precipitated plastics were removed when centrifuged in a JA-17 rotor (6000 rpm, 20 minutes), model Beckman J2-21. The last plastic residuals were filtered off using polypropylene (0.45 µm) syringe filters. The produced filtrate was then diluted with nitric acid to obtain  $\times 10$  and  $\times 10^2$  and  $10^3$  dilutions and filtrated once more with a 0.45 µm filter to obtain a suitable sample to use in the ICP – OES. The test was performed in triplicate.

### **5.3 Determination of the antimony distribution in a cross section of ABS**

To determine the acids leaching efficiency of the antimony it was important to evaluate how the antimony was distributed in the ABS computer housing: only on the surface or through the whole cross section. This result could then tell whether the antimony leaching treatment was only working on the surface of the test specimen. SEM-EDS was used to evaluate the cross section of an ABS test sample (20 x 3 mm). Three rows (in the top, middle and bottom) with 5 points each were investigated across the cross section, see Figure 6.4.

### **5.4 Degradation test of ABS with different gamma-irradiation doses and accelerated aging**

The aim of the test was to see if gamma-irradiation could improve the lifetime of ABS after both accelerated aging and recycling of the material. Three different samples were prepared: non-irradiated ABS, 40 kGy irradiated ABS (irradiated once at the start of the test) and 10 kGy ABS (irradiated between each cycle, giving a total dose of 40kGy).

The plastic granulate and flakes (depending on the stage in the recycling cycle) were irradiated in the Gammacell 220. All the recycling cycles had the same setup: gamma-irradiation, drying, extrusion of strips, grinding plastics flakes and then aging. However, at cycle 1-4 the drying step was excluded for all samples, the non-irradiated ABS had no gamma-irradiation at all and the 40 kGy sample only once in cycle 0.

The extrusions were performed by a Collin extruder 3250-09-88, (screw length 694 mm, screw diameter 25 mm and rotational velocity 50 rpm for all extrusions). The extruder was heated at three zones along the cylinder, one at the adapter and one at the die and had the temperature profile 200, 200, 200, 210 and 210 °C. The die was of slit type with an opening of 50 x 0.09 mm and gave strips that were 1.0-1.1 mm thick and 32-33 mm wide.

Prior to extrusion, the materials were dried at 80 °C for 4 h in air in a Heraeus oven, type UT 5042. The aging was performed in the same oven at 90 °C for 144 h with constant air flow of 72 L min<sup>-1</sup>. At 72 h ( $\pm$  3 h), the ABS flakes were taken out and shaken to make sure that the oxygen was evenly distributed in the top and bottom of the glass beakers.

The cutting of the strips was done by a granulator of model SG 10 Ni from Dreher. The produced flakes had a size of approximately 3.5-4.5 x 32-33 mm. Samples were collected after each extrusion occasion for further aging and recycling. Extruded strips were also collected after each cycle for tensile testing. The test specimens, in the shape of dog bones, were punched out from the strips with manually handled punching equipment connected to a punch with the ISO standard ISO-527-5A. The test specimens were conditioned at 25 ( $\pm$  2) °C and 50 ( $\pm$  5) % relative humidity for a minimum of 24 h prior the tensile test.

The tensile test was performed on a Zwick 4031 with an Instron load cell (500 N) together with the testXpert software. The equipment was used with a tensile speed of 2.8 mm min<sup>-1</sup> (approximately 10% of the length of the waist of the dog bone). An additional test was performed with different tensile speeds (5.6, 28, 280 and 560 mm min<sup>-1</sup>) to see if the material showed a ductile to brittle transition, i.e. became more brittle with increased tensile speed.

In parallel with the manually punched test specimens, another set of test specimens was produced in an injection moulding machine, Arburg Allrounder 221 M 250-55 (maximum clamp force 250 kN, manufactured in 1996), to compare possible variations in the test results within each test.

For the 'Effect of gamma-irradiation dose on ABS test', the tensile tests were performed on materials from cycle 0, thus, they had not been aged, with the investigated irradiation doses of 0, 10, 50 and 400 kGy.





## 6 Results and discussion

### 6.1 Composition analysis of mixed WEEE plastics

The number of different kinds of materials found in the different batches, see Table 6.1, is what can be expected from mixed WEEE. Some 25-30 different types of plastics are usually mentioned in articles. The main plastic constituents were PS/HIPS (42 %) and ABS (38 %). PP also had a fairly big share at 10 %.

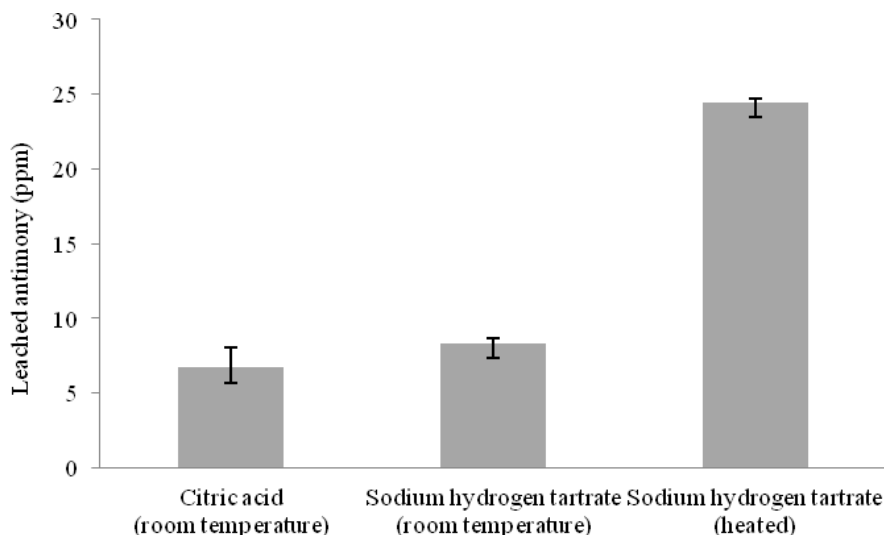
**Table 6.1.** Summary of flake size and amount of analysed material in the three investigated batches the standard deviation is stated in brackets.

Batch	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

### 6.2 Leaching of antimony with citric and tartrate acid and/or DMSO

#### 6.2.1 Pre-test of leaching acids on fly ash

The highest leaching content of antimony was in heated sodium hydrogen tartrate, as can be seen in Figure 6.1. The citric acid was not as efficient as what Hansen et al [40] noticed in their experiment with the citrus fruit juices that leached Sb from the PET bottles into the beverages. Heated sodium hydrogen tartrate solution was three times more able to leach antimony than at room temperature. For the following tests it was decided that heated sodium hydrogen tartrate should be tested on the computer plastics together with DMSO. The statistics is calculated with the uncertainty propagation method (the error is calculated in each step and summed up in the end) on the experimental handling except for the test method. Other error sources such as the sampling of the ash etc were outside our control.



**Figure 6.1.** Leached antimony from fly ash.

### 6.2.2 Elemental analysis of computer plastic

To calculate the antimony leaching efficiency of the acids, the total elemental levels were investigated in the ABS (computer plastic). Not surprisingly for an ABS plastic, the carbon, hydrogen and nitrogen levels were high. There were also other, not identified, elements stated under the ‘Other’ column that may be oxygen and/or inorganic fillers like calcium carbonate ( $\text{CaCO}_3$ ) and/or titanium dioxide ( $\text{TiO}_2$ ).

**Table 6.2.** Element levels (%) in the computer plastic.

Element	C	H	N	Br	Sb	Other
Content (%)	70.8	6.7	4.4	9.6	4.8	3.6

The samples were made in duplicate and the accuracy of the test method was  $\pm 0.30$  % absolute.

### 6.2.3 Amount of antimony leached from computer plastic by different media

It is clear that the combination of DMSO and sodium hydrogen tartrate was the working leaching media. Pure DMSO, sodium hydrogen tartrate in water and water alone did not work as leaching media for antimony. The tartrate is needed as it binds to the Sb and forms an anionic (negatively charged) complex with it. This keeps the Sb in solution. Without the tartrate the most stable form of the Sb will be as insoluble  $\text{Sb}_2\text{O}_3$ . Depending on the exact form of the  $\text{Sb}_2\text{O}_3$  (there are two forms; valentinite and senarmonite) if all the Sb is present as one form of  $\text{Sb}_2\text{O}_3$  then a second

leaching will recover more Sb. But if two forms of  $\text{Sb}_2\text{O}_3$  are present and one is harder to dissolve than the other, then it is possible that the second leaching will not recover any more Sb from the waste plastic [51, 52]. Sodium hydrogen tartrate in DMSO could leach antimony while sodium hydrogen tartrate in water could not. This can be explained by the fact that the DMSO dissolves the plastic completely and the antimony situated in the bulk can be leached.

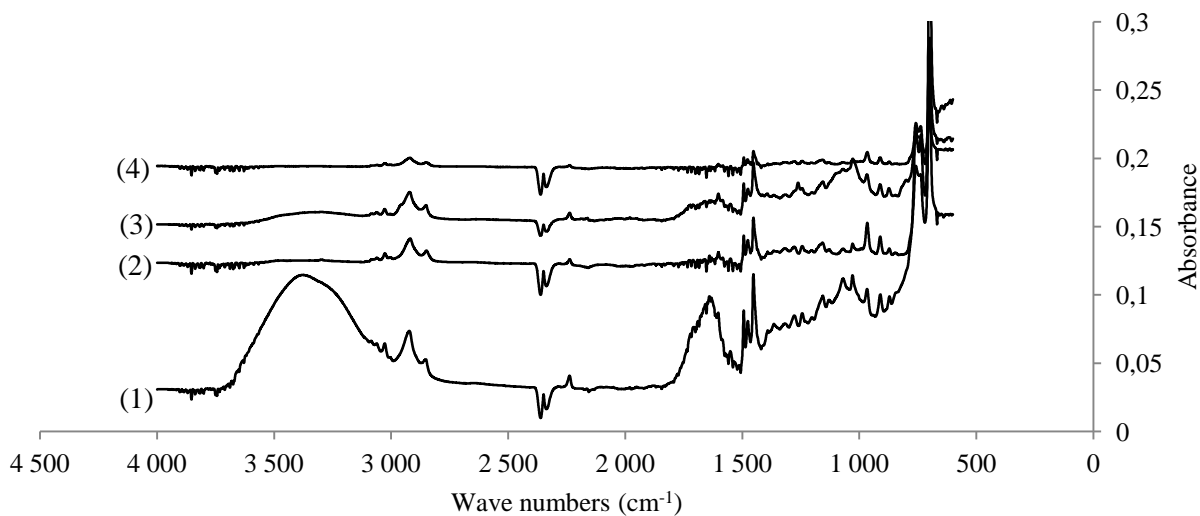
**Table 6.3.** Leached antimony (%) from computer plastic using different leaching media.

Leaching medium	Sodium hydrogen tartrate in DMSO	DMSO	Sodium hydrogen tartrate in water		Water
Leaching condition	Heated	Heated	Room temperature	Heated	Room temperature
Antimony leaching (%)	47.9	0	0	0	0

Comparing this result with other work done in the industry, the Centrevap process [42] should be mentioned. This process was developed within the Waste Resources Action Programme (WRAP). It was developed after the Creasolv® process, developed by Fraunhofer Institute IVV in cooperation with CreaCycle GmbH, which is used for removing BFR in styrene plastics. The aim of the Centrevap process was to remove both BFR and impurities such as  $\text{Sb}_2\text{O}_3$ , fillers, pigments and stabilizers from the styrene based plastic HIPS. Ground plastics are dissolved in toluene and the suspension (heated to 65 °C) is then pumped through a filter and centrifuges. The removed particles, un-dissolved plastics, metals and fillers from the dissolved plastics and any un-dissolved BFR and  $\text{Sb}_2\text{O}_3$  are further processed to a dry powder where the toluene is evaporated. The powder is then melted and extruded where the polymer is pelletized and contains less than 1 % solvent. The result from their tests showed however that the bromine removal content was not sufficiently high though the antimony removal level was almost 60 % [42]. Relating that figure with our result of almost 50 % leaching efficiency for antimony, with a non-optimised method, is encouraging news.

#### 6.2.4 Structural stability

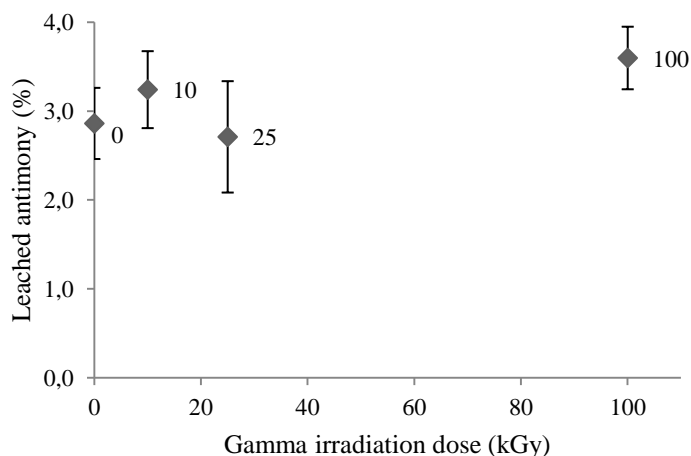
The structures of the computer plastic were examined by FTIR-ATR to ensure the mechanical properties were maintained after the acid treatment, on the surface as well as in the bulk of the computer plastic. The nitrile peak at  $2250\text{ cm}^{-1}$  is only negligibly influenced by the sodium hydrogen tartrate solution (surface) (1) compared with the untreated computer plastic (surface) (3), as can be seen in Figure 6.2. Small differences can be distinguished between the surface and the bulk of the sodium hydrogen tartrate-treated (1 and 2) and the untreated (3 and 4) computer plastic. The sodium hydrogen tartrate treatment only has a minor effect on the polymer itself. The absence of carboxylic acid ( $1700\text{ cm}^{-1}$ ) and carboxylate anions ( $1600\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ ) indicates that very little, if any, hydrolysis of the nitrile groups has taken place. Thus, little, if any degradation of the plastic has occurred. The broad peak at  $3400\text{ cm}^{-1}$  for (1) and to some extent (3) is explained by water or other O-H bonds.



**Figure 6.2.** FTIR-ATR spectrum comparison for sodium hydrogen tartrate solution on the surface (1), sodium hydrogen tartrate solution in bulk (2), untreated computer plastic on the surface (3) and untreated computer plastic in bulk (4).

#### 6.2.5 The effect of gamma-irradiation on antimony leaching

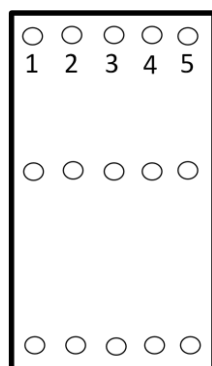
Gamma-irradiation was also tested to see if it would increase the antimony removal from the computer plastic. As can be seen in Figure 6.3, the irradiation had no significant effect on the antimony leaching. Thus, gamma-irradiation will most probably not be used in a future antimony removal process. The statistics was calculated with the uncertainty propagation method (the error is calculated in each step and summed up in the end) on 3 replicates for each irradiation dose.



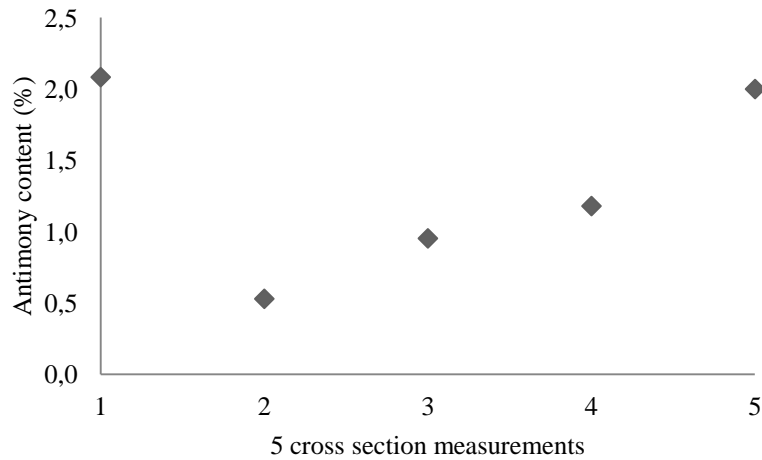
**Figure 6.3.** The influence of gamma-irradiation on antimony leaching from computer plastic using sodium hydrogen tartrate with DMSO as the solvent.

### 6.3 Determination of the antimony distribution in a cross section of ABS

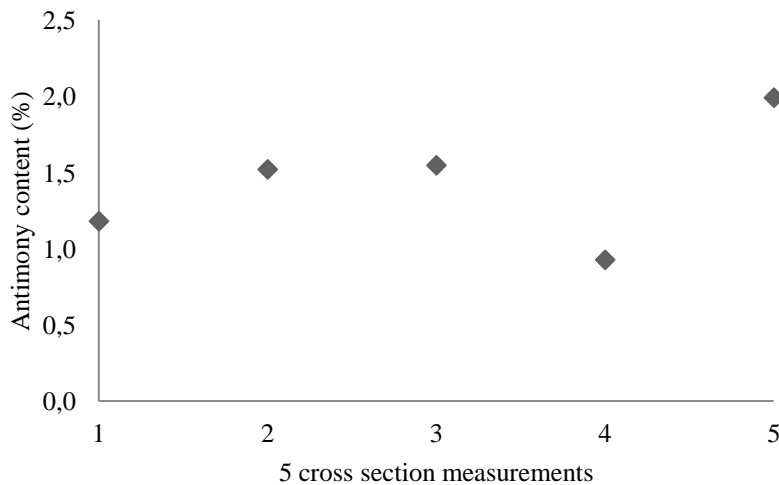
As shown in Figure 6.5 and Figure 6.6, it was difficult to see any significant difference in the antimony distribution in the cross section of a piece from the computer housing. Nor could a difference be seen between the untreated and the tartrate acid-treated sample. Although, for the untreated sample it seemed like the antimony content was lower in the middle of the cross section, number 3 in Figure 6.4 and equally high at the edges (number 1 and 5 in Figure 6.4). This could possibly be explained by the fillers and additives in plastics tending to migrate towards the surface with time and degradation of the plastics.



**Figure 6.4.** Top view of the five measurement points for antimony content measurements (at the top, middle and bottom) through the cross section of a plastic piece.



**Figure 6.5.** The average profile of antimony content from five measurements throughout the cross section of an untreated ABS plastics piece.



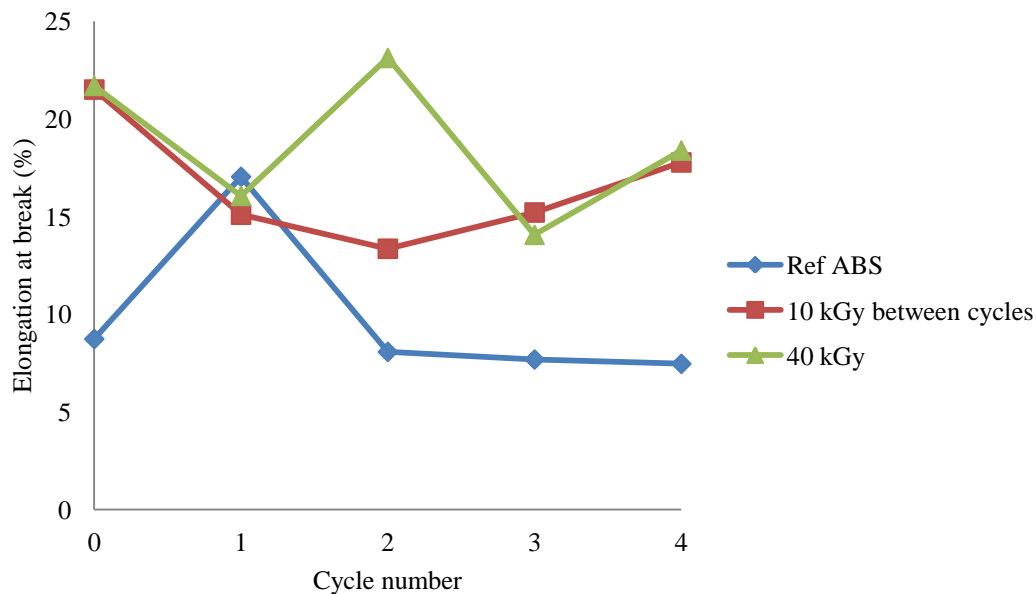
**Figure 6.6.** The average profile of antimony content from five measurements throughout the cross section of a tartrate-treated ABS plastics piece.

## 6.4 Degradation test of ABS with different gamma-irradiation doses and accelerated aging

### 6.4.1 Elongation at break

The variation in elongation at break (EB) gave the idea that surface cracks were created when the dog bones were punched out from the extruded strips. A comparison test was executed with injection moulded dog bones of similar size and thickness. The result showed that the variation was similar to the injection moulded dog bones, the only difference being that the elongation at

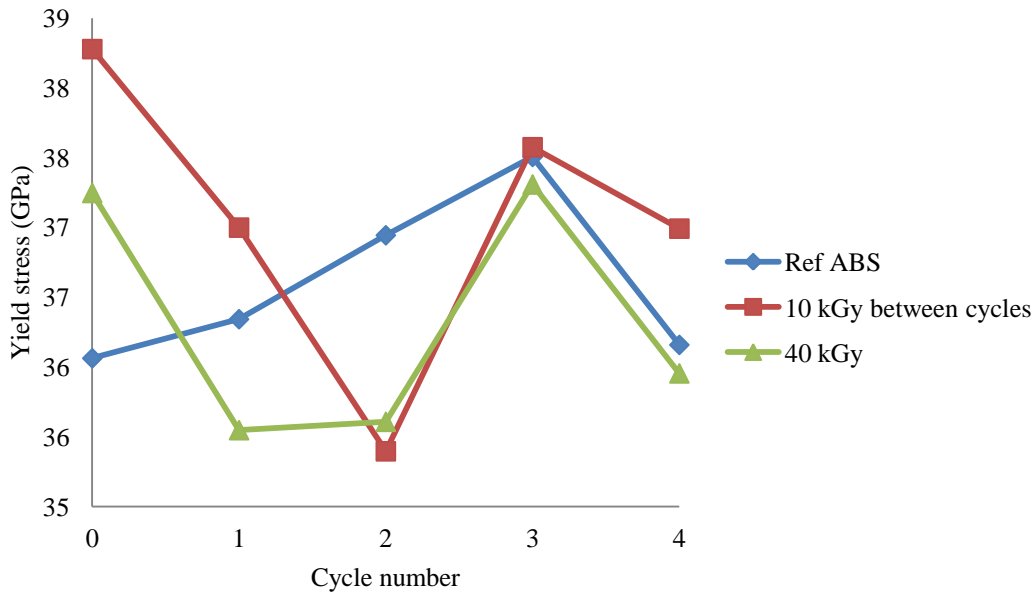
break was higher overall. This can be explained by the higher orientation of the polymer chains in the injection moulded test specimens. The hypothesis was that the gamma-irradiation would prevent the degradation of the ABS during the accelerated aging test. Previous results presented by Boldizar and Möller [53] indicated that the elongation at break increased for each cycle in the extrusion steps up until cycle 6. Unfortunately for our test, the standard deviation was very high and therefore no justified conclusions could be drawn from the results on EB, even though there seem to be similar behaviour between the 10 kGy (gamma-irradiated between each cycle) samples and the 40 kGy samples. They tend to have higher elongation at break than the reference ABS samples which can be seen in Figure 6.7.



**Figure 6.7.** Elongation at break (%) comparison between Reference ABS, 10 kGy between each cycle and 40 kGy gamma-irradiated material.

#### 6.4.2 Yield stress

No real trends could be discerned for the yield stress results. The standard deviation was lower than for the EB, yet still too high to be reliable. Nevertheless, it seems like the reference ABS increasing with time even cycle 3 and then decreases in cycle 4, see Figure 6.8.

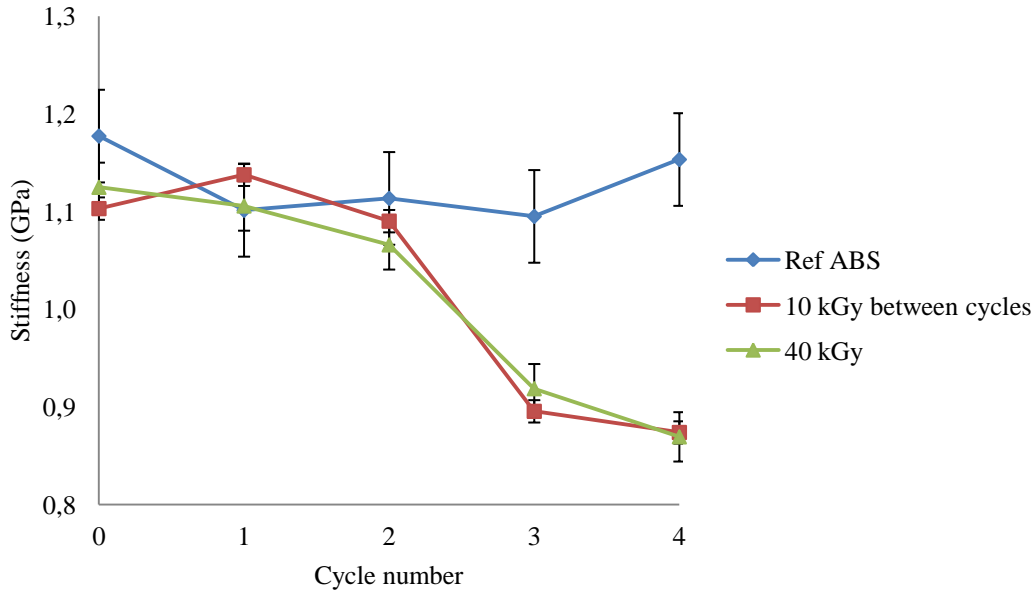


**Figure 6.8.** Yield stress comparison (GPa) between the Reference ABS, 10 kGy between each cycle and 40 kGy gamma-irradiated materials.

### 6.4.3 Stiffness

A significant difference could be noticed in the change in stiffness during the simulated recycling cycles. After cycle 2, it can be seen in Figure 6.9 that the gamma-irradiated samples got a lower stiffness than the non-irradiated sample contradictory to the hypothesis that the stiffness would increase, as shown by Perraud et al [54] when irradiating nitrile rubbers and generating crosslinking, giving higher stiffness. The reason for this decrease in the gamma-irradiated samples is not yet fully understood and there might be a reason for further investigation of the event.





**Figure 6.9.** Stiffness comparisons (GPa) between the Reference ABS, 10 kGy between each cycle and 40 kGy gamma-irradiated materials.

The standard deviation is calculated on five test specimens per material and shown in Figure 6.7-6.9 with one  $\sigma$ , thus a probability of 68 %.

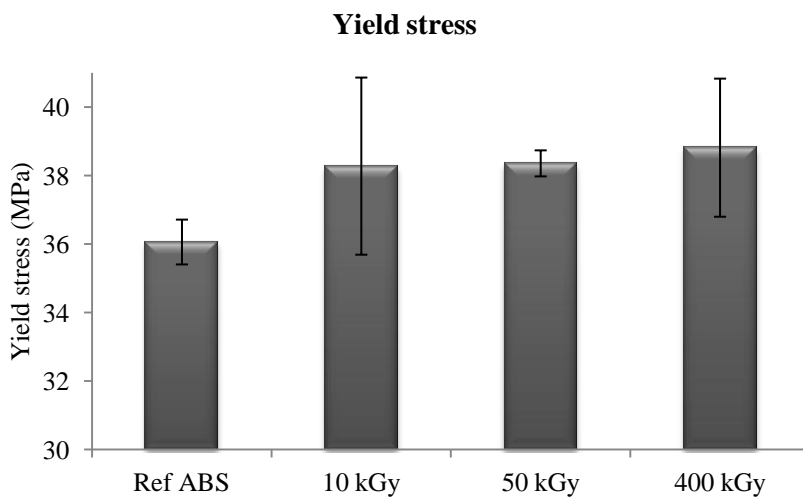
#### 6.4.4 The effect of a gamma-irradiation dose on ABS

Excluding the 10 kGy sample, it seems to be a decrease in the stiffness with increasing irradiation dose, see Figure 6.12 which is also supported by Figure 6.9. This is contradictory to the results Perraud et al found [54]. They saw an increase in stiffness for the hydrogenated nitrile butadiene rubber (HNBR), an elastomer commonly used in the automotive and printing industries (including two parts of the ABS; A- and B-), when it was irradiated with an electron beam. Also the tensile strength decreased in their test while it is similar for our different irradiation doses. However, the elongation at break did decrease with increasing irradiation dose, which was the same behaviour as we noticed in our test.

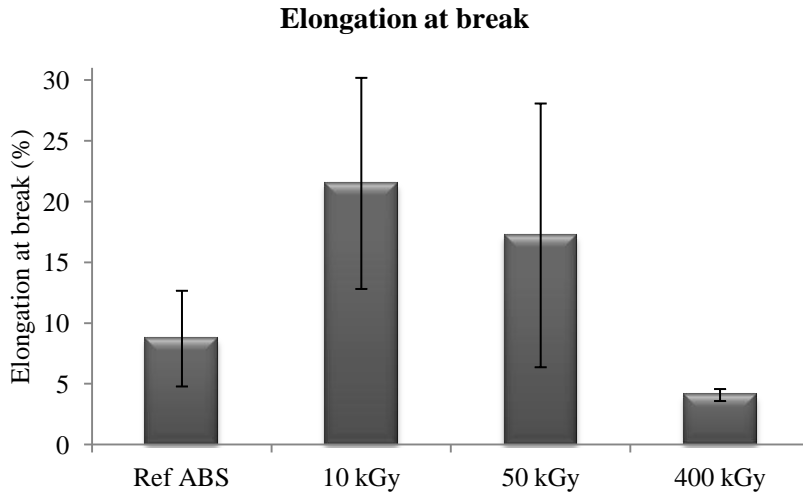
The acrylonitrile content has shown to influence how sensitive it is to gamma-irradiation. Cardona et al analysed acrylonitrile butadiene rubber and saw an increased effect of the irradiation with increasing acrylonitrile content. Moreover, the acrylonitrile part was more sensitive to gamma-irradiation than the butadiene part and lastly, the reactions observed were the consumption of double bonds and crosslinking, no chains scissoring occurred [55]. This

behaviour can explain the increase in viscosity noticed in our comparison of non-irradiated and gamma-irradiated ABS. A trend towards tougher material with an increasing irradiation dose can be noticed for the yield stress in Figure 6.10.

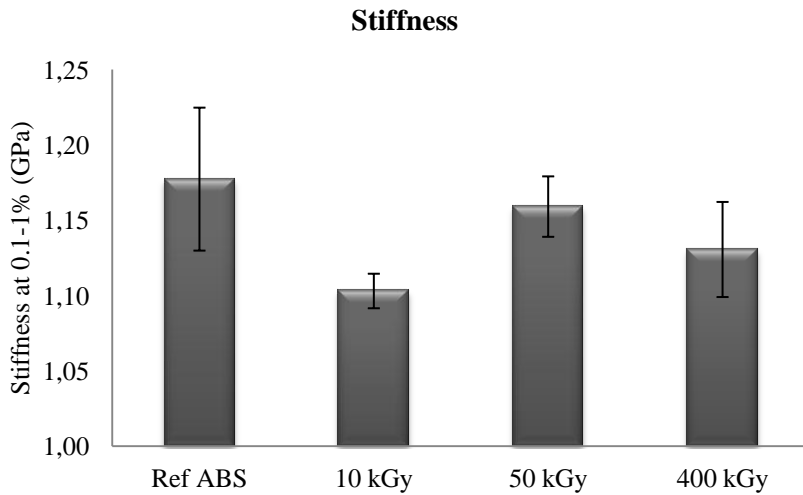
The ABS is able to tolerate a gamma-irradiation dose of at least 400 kGy, this dose compares well with the low dose rate radiation resistance studies of phenolic resins by Gilfrich et al [56]. They subjected phenolic resins to doses of between 100 kGy and 2 MGy of  $^{60}\text{Co}$  gamma-irradiation at  $15 \text{ Gy hr}^{-1}$ . It was found that a dose of 200 kGy delivered under these conditions caused negative effects on the physical properties of the plastic. In contrast more than 1 MGy of electron beam irradiation ( $100 \text{ MGy hr}^{-1}$ ) was required to cause similar changes. Similar results were reported by Gilfrich et al for melamine-formaldehyde plastics [57].



**Figure 6.10.** The effect of gamma-irradiation (non-irradiated, 10, 50 and 400 kGy) on ABS yield stress.



**Figure 6.11.** The effect of gamma-irradiation (non-irradiated, 10, 50 and 400 kGy) on ABS elongation at break.



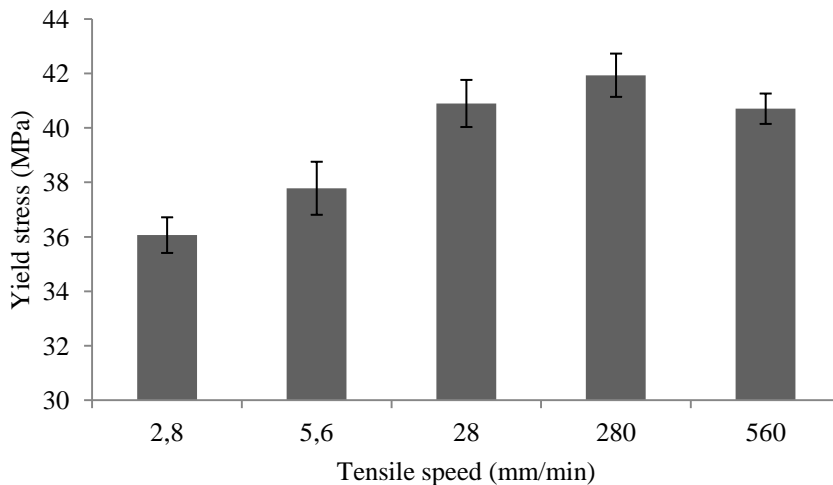
**Figure 6.12.** The effect of gamma-irradiation (non-irradiated, 10, 50 and 400 kGy) on ABS stiffness.

The standard deviation is calculated on five test specimens per irradiation dose and shown in Figures 6.10-6.12 with one  $\sigma$ , thus a probability of 68 %. All the five stress/strain curves for each material are shown in Appendix B.

### 6.4.5 Ductile to brittle transition test

No ductile to brittle transition was seen with respect to strain rate. The samples showed plastic deformation (necking) before breakage, which did not appear to have any correlation with the tested strain rates. The absence of a brittle to ductile transition is possibly due to the multi-component system of ABS with the rubber component, which is not very sensitive to the strain rates used in this test [58].

It seems to be a trend of increasing yield stress in Figure 6.13 valid for all tensile speeds except the last, at 560 mm/min, which is a very high tensile speed.



**Figure 6.13.** The effect of tensile speed (mm/min) on yield stress (MPa) for ABS.

The standard deviation is calculated for five test specimens per tensile speed and shown in Figure 6.13 with one  $\sigma$ , thus a probability of 68 %.

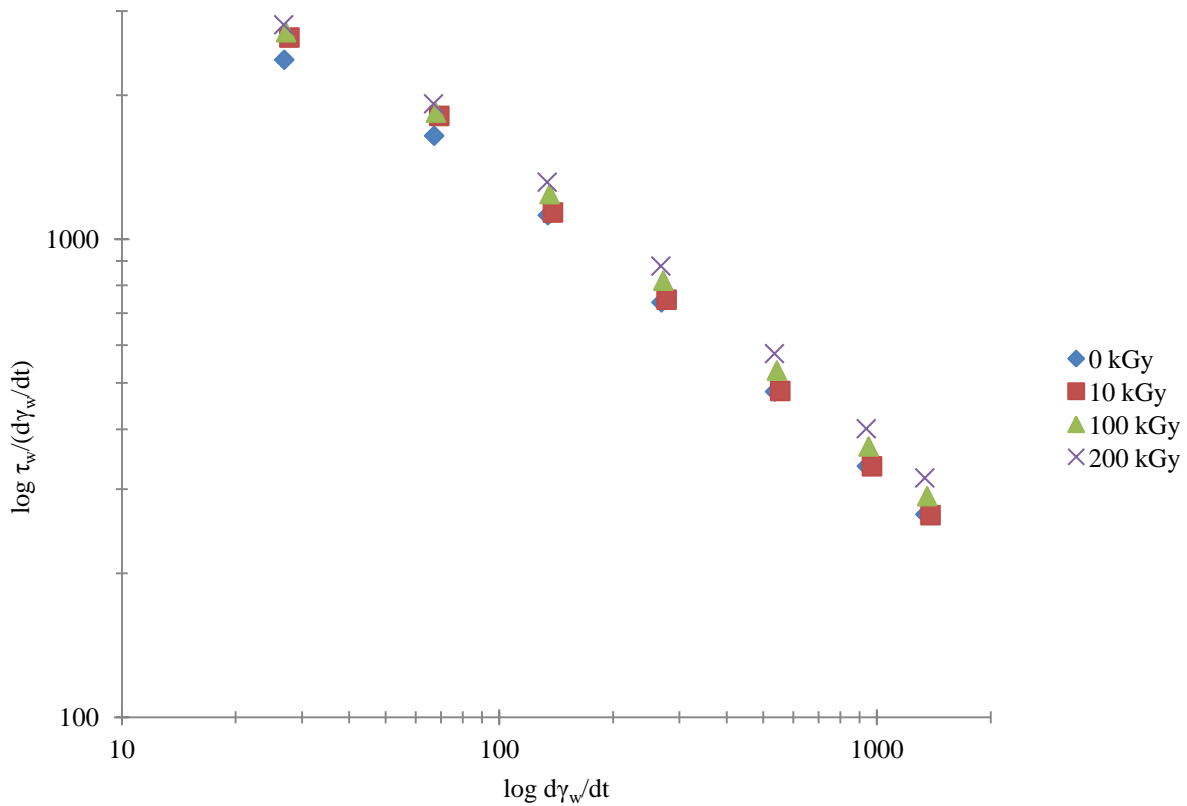
### 6.4.6 Viscosity comparison of non-irradiated and gamma-irradiated ABS

An effect of the gamma-irradiation could be seen on the ABS viscosity in Table 6.4 and Figure 6.14 and it increased with increasing irradiation dose. The most likely occurrence is that the ABS has crosslinked as has been seen in other studies made by Cardona et al and Perraud et al [54, 55].

**Table 6.4.** Viscosity data of ABS treated with different gamma-irradiation doses.

	0 kGy	10 kGy	100 kGy	200 kGy
Shear rate ( $s^{-1}$ )	Viscosity (Pas)	Viscosity (Pas)	Viscosity (Pas)	Viscosity (Pas)
20	341462	380075	389915	404241
50	236824	260605	264854	276233
100	161569	163664	178863	189391
200	106181	107555	117884	126453
400	69110	69309	76467	82957
700	48262	48222	53048	57790
1000	38263	38104	41756	45586
1500	29257	29013	31744	34727

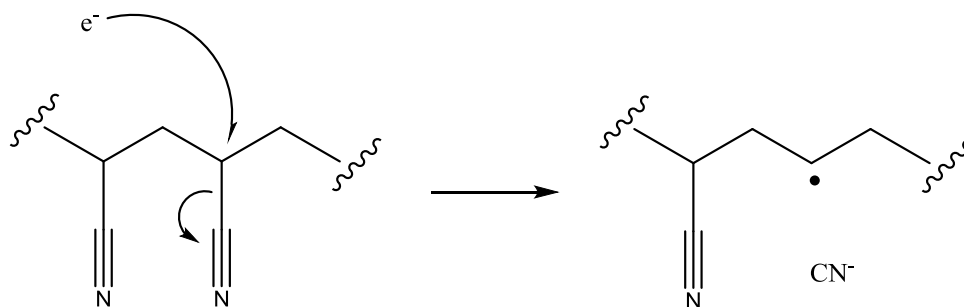
Combining the viscosity curves in the same graph shows that the viscosity has increased with increasing gamma-irradiation dose; see Figure 6.14. 0 and 10 kGy has similar values, especially for higher shear rates while the 100 kGy line is in between the 10 and 200 kGy lines.



**Figure 6.14.** Summary of the viscosities for non-irradiated ABS, 10, 100 and 200 kGy gamma-irradiated ABS.

PVC and PAN have some similarities. Both polymers are formed from monosubstituted ethylenes. PAN is build-up by a mixture of monomers of acrylonitrile and is, as mentioned before, the A-part in ABS.

A leaving group is an atom or molecule which can leave a molecule with electron pairs, for example the iodide anion leaving from iodomethane. PVC and PAN are both chains of  $\text{CH}_2$  groups which alternate with  $\text{CHX}$  groups (X is either a chlorine atom or a cyanide group). The C-X bonds can be broken, for example by the reaction of a solvated electron with the carbon bearing the X group, the C-X bond is broken (both electrons in the bond go to the X group) forming a  $\text{X}^-$  anion and a carbon centred free radical, described in Figure 6.15.



**Figure 6.15.** The formation of a polymer free radical by the reaction of a solvated electron with polyacrylonitrile.

Marcella et al reported that when di-(2-ethylhexyl)-phthalate plasticized PVC blood bags were irradiated with high energy X-rays (25 to 100 kGy from a LINAC) the plasticizer was less able to leach out of the plastic. This decrease in the rate of leaching can be rationalised by the fact that a crosslinked polymer is less able to swell in cyclohexane and allow the phthalate ester to diffuse out. García-Castañeda et al [59] reported that electron beam irradiation (50 to 100 kGy) of PVC caused crosslinking which improved the physical properties at temperatures between 70 and 95  $^{\circ}\text{C}$ . Similar results were reported in the same paper with  $^{60}\text{Co}$  gamma-irradiation. It is interesting to note that at similar irradiation doses to those used in this thesis in common with the ABS the PVC was improved by crosslinking.

## 7 Conclusions

From the ‘antimony leaching from ABS computer housing experiment’ it was shown that heated sodium hydrogen tartrate in DMSO is an efficient leaching medium for antimony recovery from ABS plastics used in WEEE. The efficiency was estimated to be 50 %. The remaining plastics can be taken care of and recycled, possibly with intermixed virgin ABS material. The DMSO in sodium hydrogen tartrate can be recovered and used again as a leaching medium. It was shown that neither water nor DMSO alone could leach any antimony; tartrate on the other hand was found to leach antimony from the ABS plastic. Sodium hydrogen tartrate in DMSO did leach antimony while sodium hydrogen tartrate in water did not at all. Sodium hydrogen tartrate is three times more efficient as a leaching medium when it is heated compared with room temperature sodium hydrogen tartrate leaching solvent.

The gamma-irradiation of the ABS before acid leaching did not show any significant leaching effect on the antimony and will therefore not be considered in a future antimony removal process. The computer plastic has not degraded notably after the sodium hydrogen tartrate treatment according to the FTIR ATR analysis.

When it comes to the mechanical properties of multi-recycled, accelerated aged and gamma-irradiated ABS, a difference could be seen in the stiffness results between the different cycles and between the different irradiation doses. The ABS non-irradiated sample was stable during all four recycling cycles and did not seem to degrade during the multi-recycling and accelerated aging. Although, the 10 kGy (irradiated between each cycle) sample and the 40 kGy sample showed a decrease in stiffness after two cycles which cannot yet be explained. Due to the very high standard deviation for the elongation at break no relevant conclusions could be drawn from the test. For the yield stress test no trend could be distinguished.

The 10 kGy (irradiated between each cycle) sample and the 40 kGy sample behaved similarly for all the tested properties and no conclusion could be drawn on whether the material would degrade less for a repeated small dose of gamma-irradiation between each recycling cycle than for a higher dose prior to the repeated recycling.

The gamma-irradiation had an influence on the mechanical properties for ABS. The ABS seems to crosslink with an increasing irradiation dose, which could be seen as the decrease in EB and higher yield stress compared to the non-irradiated ABS. The high variation in the EB results may be explained by the structure of ABS: the butadiene rubber part. It seems to be almost a

randomized event if the ABS sample breaks or elongates further. It does not seem likely that the punching of the dog bones from the test strips has caused any major surface damage to the samples that can explain this high variation in the EB test results. The comparison with the injection moulded test specimens supported the theory since the variation in EB was similar for those test specimens. A trend could be noticed towards higher yield stress with an increasing gamma-irradiation dose, and the opposite behaviour was noticed for the stiffness: a decrease in stiffness with higher irradiation dose. However, the 10 kGy sample did not fit the trend line very well, but it may be explained by its high variation within the sample.

No ductile to brittle transition was seen when increasing the tensile speed. The samples showed a plastic deformation (necking) before breakage that did not appear to have any correlation with the tested strain rates. The absence of a brittle to ductile transition with respect to strain rate is possibly due to the multi-component ABS system with the rubber component, which is relatively insensitive to the high strain rates used in this test.

Gamma-irradiation did also influence on the rheological properties or for the mechanical properties; the viscosity increased with increasing irradiation dose.



## **8 Future work**

Investigate how different combinations of physical- and reactive compatibilization strategies influence a WEEE plastics blend and understand how gamma-irradiation influences these compatibilization strategies. The efficiencies of these compatibilizers would be interesting to evaluate on a WEEE plastics blend, possibly also in combination with other compatibilization strategies. Get a deeper understanding on what is happening on molecular level when irradiating waste plastics.

It would also be very interesting and stimulating to collaborate even further with recycling companies and investigate how their blended rest fractions can be recycled.



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I would like to thank:

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## 11 List of abbreviations

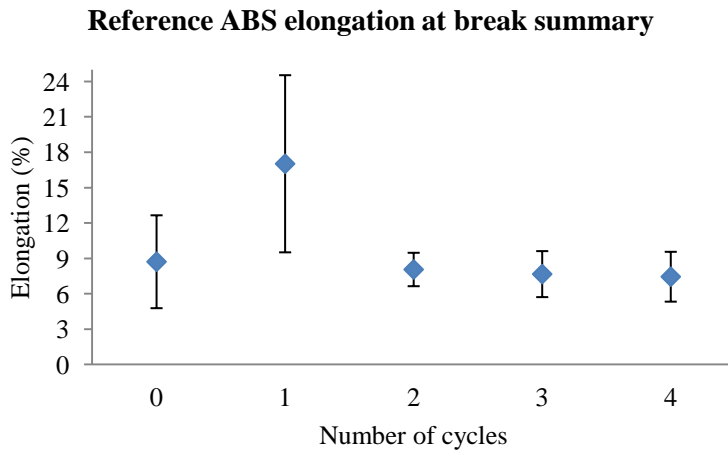
ABS	Acrylonitrile butadiene styrene
Ag	Silver
Au	Gold
BFR	Brominated flame retardants
Br	Bromine
C	Carbon
CaCO <sub>3</sub>	Calcium carbonate
CE	Consumer equipment
CHN	Carbon hydrogen nitrogen
CO <sub>2</sub>	Carbon dioxide
CRT	Cathode ray tube
CQ	Camphorquinone
DFG	German Research Foundation
DMSO	Dimethyl sulfoxide
EB	Elongation at break
EEE	Electrical and electronic equipment
EPA	United States environmental protection agency
EU	European Union
FR	Flame retardants
FTIR – ATR	Fourier transform infrared spectroscopy – attenuated total reflectance
GC – MS	Gas chromatography – mass spectroscopy
H	Hydrogen
H <sub>2</sub> O	Water
HIPS	High impact polystyrene
HNBR	Hydrogenated nitrile butadiene rubber
ICP – OES	Inductively coupled plasma – optical emission spectroscopy
ICT	IT and telecommunications equipment
LCD	Liquid crystal display

LLDPE	Linear low density polyethylene
MIR	Mid IR
MSW	Municipal solid waste
N	Nitrogen
NASA	National aeronautics and space administration
Ni	Nickel
PAN	Polyacrylonitrile
Pb	Lead
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
Pyrolysis – GC	Pyrolysis – gas chromatography
RoHS	Restriction of hazardous substances
Sb	Antimony
Sb <sub>2</sub> O <sub>3</sub>	Antimony trioxide
SEM – EDS	Scanning electron microscope – energy dispersive spectroscopy
TiO <sub>2</sub>	Titanium dioxide
WEEE	Waste electrical and electronic equipment
XRF	X-ray fluorescence
Zn	Zinc
γ	gamma

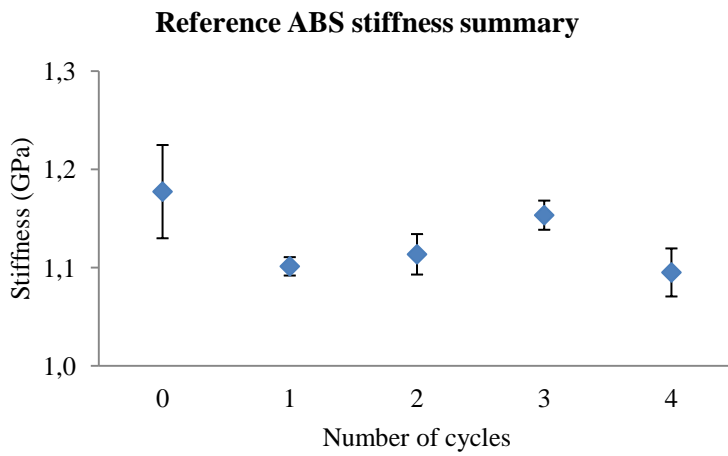
## 12 Appendices

### Appendix A

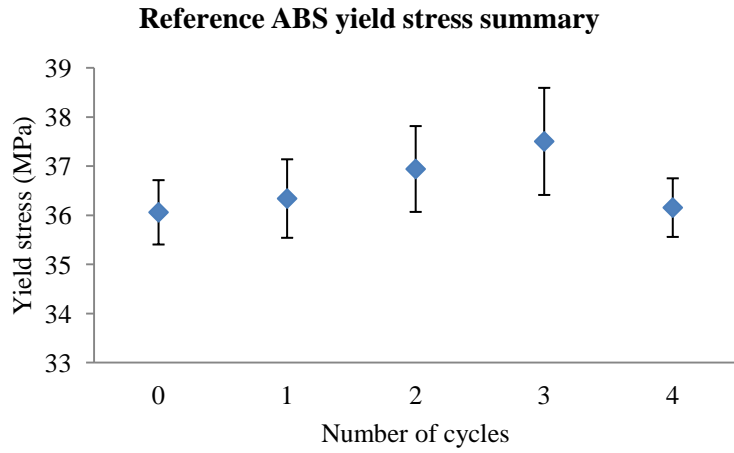
Summary of tensile tests for non-irradiated ABS, 10 kGy between each cycle and 40kGy, cycles 0-4.



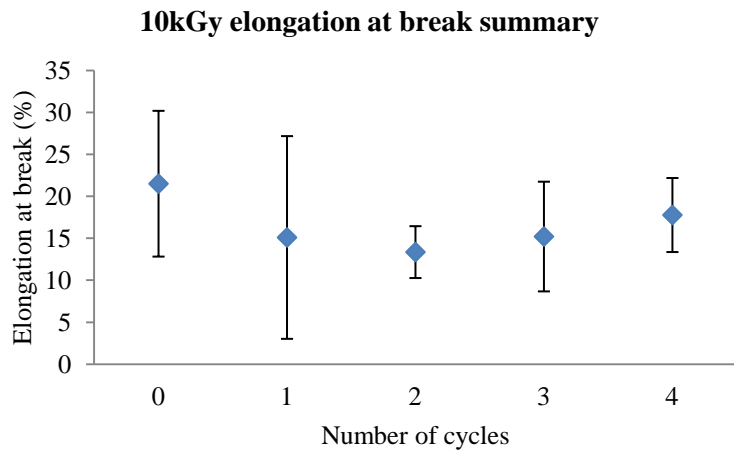
**Figure A.** Summary of elongation at break for reference ABS, cycle 0-4.



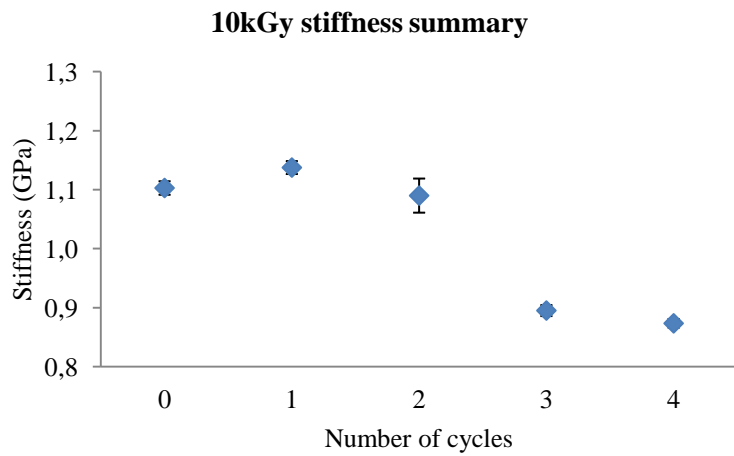
**Figure B.** Summary of stiffness for reference ABS, cycle 0-4.



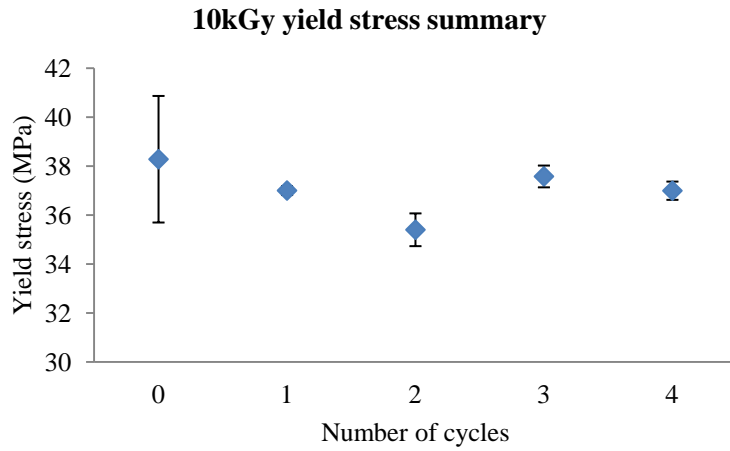
**Figure C.** Summary of yield stress for reference ABS, cycle 0-4.



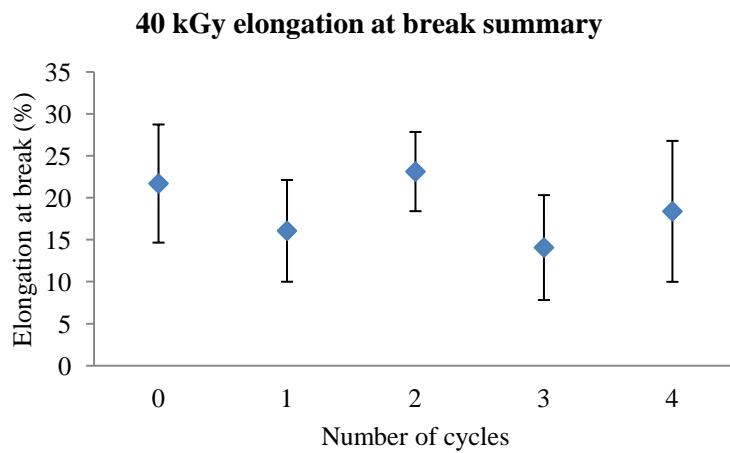
**Figure D.** Summary of elongation at break for 10 kGy between each cycle, cycles 0-4.



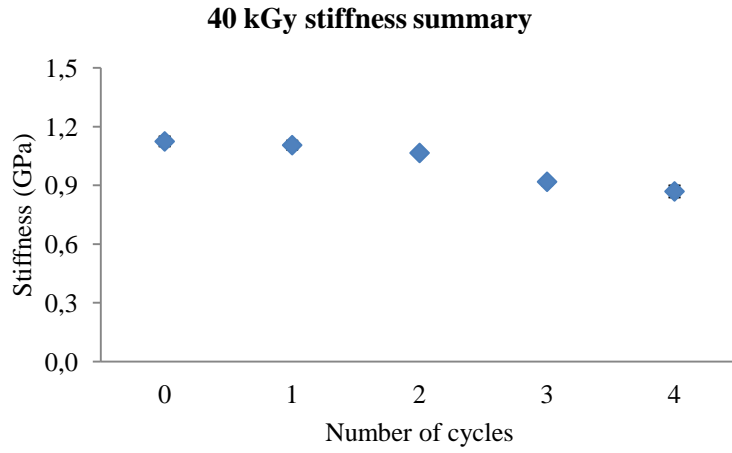
**Figure E.** Summary of stiffness for 10 kGy between each cycle, cycles 0-4.



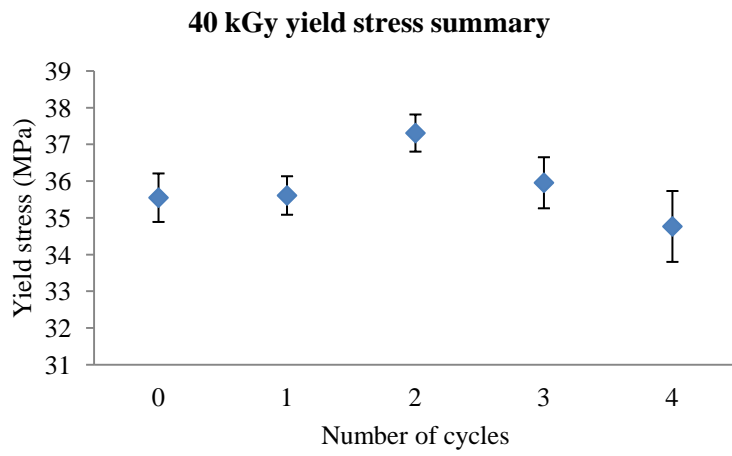
**Figure F.** Summary of yield stress for 10 kGy between each cycle, cycles 0-4.



**Figure G.** Summary of elongation at break for 40 kGy, cycles 0-4.



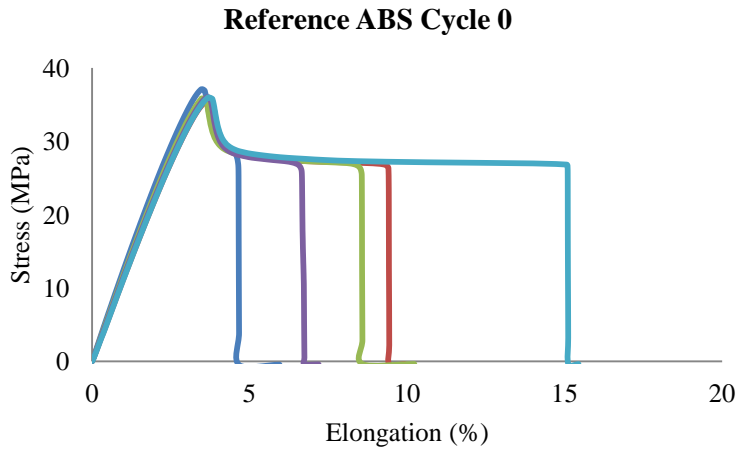
**Figure H.** Summary of stiffness for 40 kGy, cycles 0-4.



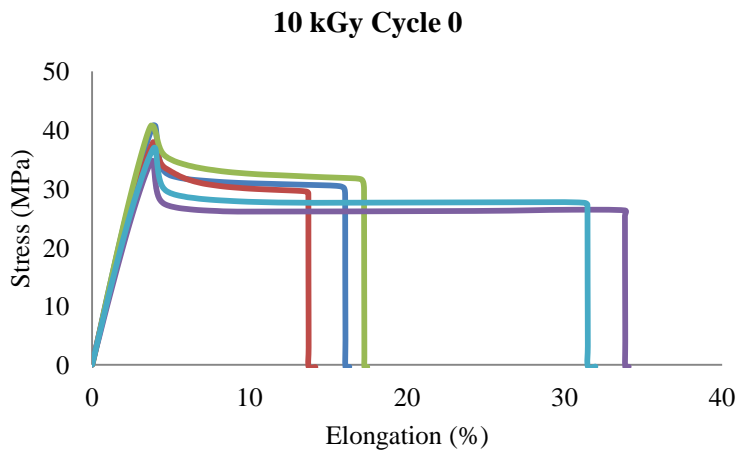
**Figure I.** Summary of yield stress for 40 kGy, cycles 0-4.

## Appendix B

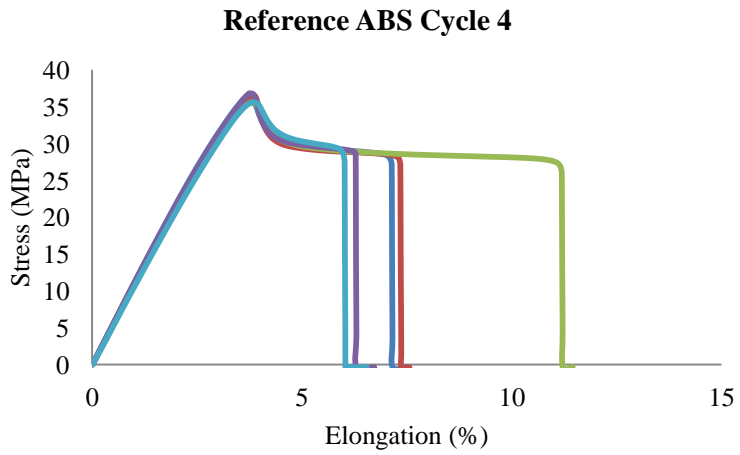
The tensile test curves (five samples per material) for cycle 0 and cycle 4 for reference ABS, 10 kGy (irradiated between each cycle) and 40 kGy. Cycle 0 for reference ABS (injection moulded test specimen), 50 kGy and 400 kGy are also included.



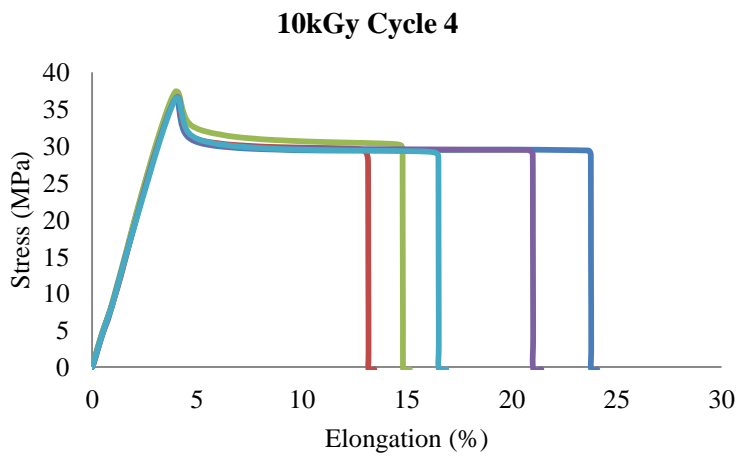
**Figure J.** Stress/strain curve for five non-irradiated ABS samples in cycle 0.



**Figure K.** Stress/strain curve for five 10 kGy samples in cycle 0.

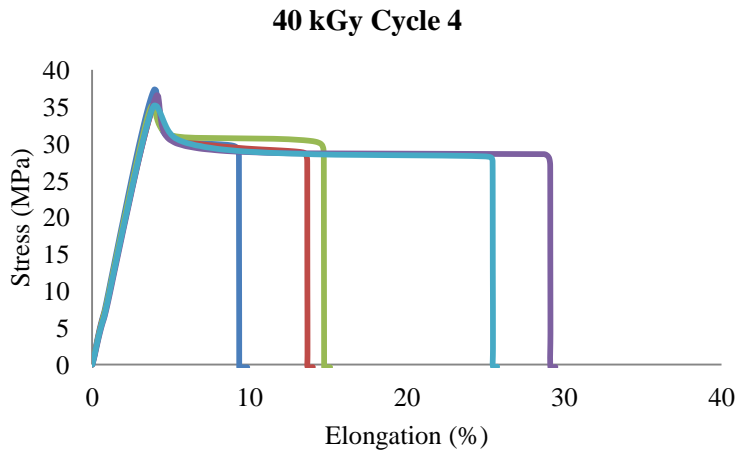


**Figure L.** Stress/strain curve for five 10 kGy samples in cycle 4.

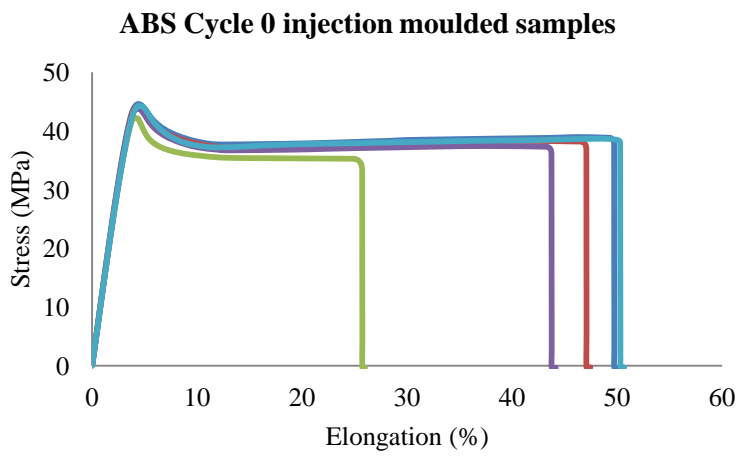


**Figure M.** Stress/strain curve for five 10 kGy samples in cycle 4.

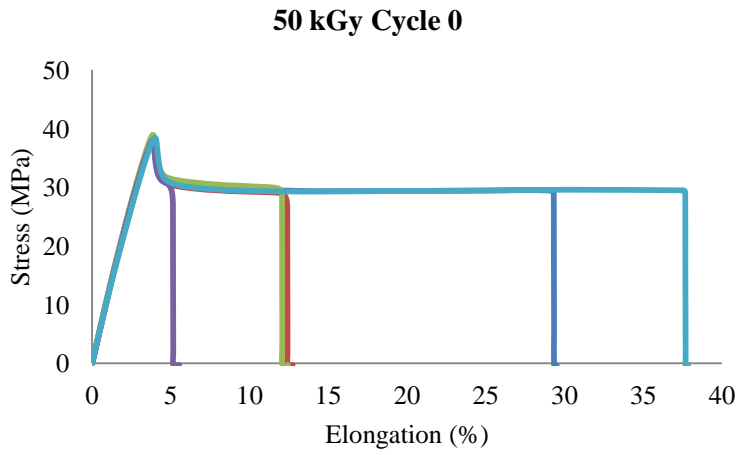




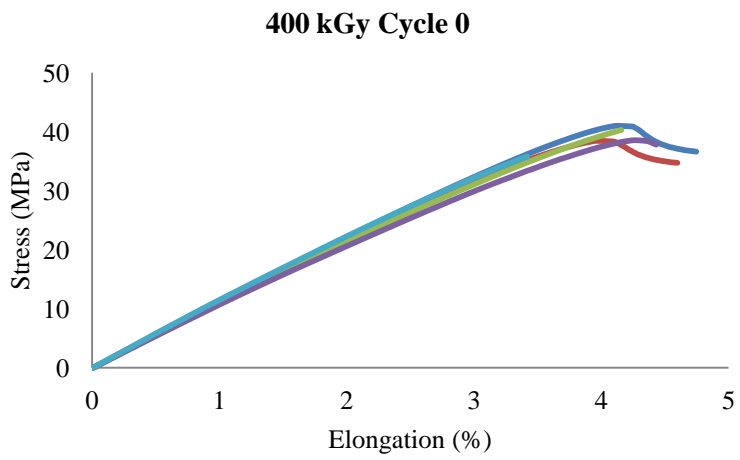
**Figure N.** Stress/strain curve for five 10 kGy samples in cycle 4.



**Figure O.** Stress/strain curve for five non-irradiated, injection moulded ABS samples in cycle 0.



**Figure P.** Stress/strain curve for five 50 kGy samples in cycle 0.



**Figure Q.** Stress/strain curve for five 400 kGy samples in cycle 0.