



Article Potential for Reuse of E-Plastics through Processing by Compression Molding

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Abstract: The amounts of e-waste, consisting of metal (e-metals) and plastic (e-plastics) streams from electronic goods, are increasing in the United States and elsewhere. The e-metals waste streams are being recycled to a reasonable degree due to the value of precious metals. E-plastic waste streams currently are not recycled or reused to a significant extent. As a result, most e-plastics are disposed of by landfilling or thermal treatment, or sent overseas for alleged recycling or reuse, any of which could result in unsafe worker exposure and release into the environment. Two of the major barriers to e-plastics' reuse or recycling are the mixed plastic content and the presence in the e-plastics of flame retardants (FR), of which two classes in particular, the brominated flame retardants (BFR) and organo-phosphorus flame retardants (OPFR), have associated health concerns. The major goal of this project is to investigate the possibility of direct reuse of e-plastics in compression molding. Preliminary data generated have identified a molding procedure that yields remanufactured e-plastics having a tensile strength of 29.3 MPa. This moderate strength level is suspected to be due to inclusions of plastic bits that did not melt and internal voids from out-gassing. Handheld X-ray fluorescence (XRF) was utilized to characterize elemental components in the e-plastics tested for compression molding. Several high "hits" for Br were found that could not be predicted visually. The preliminary XRF data for BFR and OPFR in this work are helpful for environmental and occupational hazard assessments of compression molding activities. Additionally, methods are suggested to characterize the metals, BFR, and OPFR content of the e-plastics using several different additional laboratory analytical techniques to determine the suitability for cost-effective and easy-to-use technologies.

Keywords: Waste Electrical and Electronic Equipment (WEEE); e-plastics; compression molding; recycling; flame retardants; GC-MS; XRF

1. Introduction

1.1. E-Waste

Waste material from electronics is referred to by a variety of terms including e-waste (or e-wastes) [1] and waste electrical and electronic equipment (WEEE) [2]. In 2012, the United States (US) generated at least 3.4 million tons of e-waste [3]. The amount of e-waste being generated is steadily increasing, both in the US and worldwide [4]. The e-waste stream consists of electronics items, such as computers, television and computer monitors, cell phones, printers/fax machines/scanners/ multifunctional devices, audio video devices (stereos, VCR, DVD players, *etc.*), as well as electrical items, such as household appliances [5]. The US Environmental Protection Agency (USEPA) has estimated that only approximately 25% of domestic e-waste is currently being recycled or reused [6]. At the same time, an increasing number of states are restricting or banning the landfilling of e-waste. For example, in Illinois, many e-wastes have been banned from landfills since January 2012 [7].

The e-waste stream can generally be divided into two substreams:

- (1) metals-containing wastes (e-metals), and
- (2) plastics (e-plastics).

E-metals contain valuable gold, silver, platinum, palladium, rare earths, *etc.*, for which cost-effective processes have been developed for recovery and/or recycling [8]. E-metal recovery is believed to make up most of the 25% of US e-waste that is recycled. However, too much e-plastic is still ending its useful life in a landfill or dumpsite due to a lack of materials' management. E-plastics is an abundant resource for high quality engineering resin as, on a volume basis, it is the largest component of e-wastes [9].

1.2. E-Plastics

E-plastics represent a larger fraction of the e-waste stream than e-metals, and there are significantly fewer options for their recycling or reuse. The general challenges associated with plastics recycling have been reviewed [10,11]. In addition to these general plastic recycling challenges, two of the major barriers to reuse of e-plastics are (1) the mixed nature of the plastics stream and (2) the possible flame retardant (FR) content of the e-plastics. Major types of polymers (plastics) in the e-plastics stream include acrylonitrile butadiene styrene (ABS), polyethylene (PE), polypropylene (PP), polycarbonate (PC), polyvinylchloride (PVC), high impact polystyrene (HIPS), or blends of these thermoplastics [9,12,13]. However, thermosets (epoxy and phenol formaldehyde, for instance) and elastomers are present in small quantities. Potentially useful e-plastics are all the plastic components of electrical devices except for circuit boards, which contain electronic chips, wiring, metals, and fiberglass reinforcement. Separating out the plastic components of a circuit board is cost-prohibitive. FRs have been used widely in the e-plastics for consumer electronics. FRs found in e-plastics are generally brominated flame retardants (BFR) or organophosphorus flame retardants (OPFR) [11]. The BFRs, especially polybrominated diphenyl ethers (PBDE), have received a great deal of attention due to their widespread occurrence in the environment, including the Great Lakes [12–16], and in electronic recycling facilities, as there are concerns about their toxicity and occupational exposures [17–19]. In recent years, many of the PBDEs have been phased out and replaced by other BFRs or OPFRs; however, many of the newer FRs have similar physical/chemical properties, and in many cases toxicity is still an issue. It is not clear whether the replacements BFR represent a better solution [20].

Most e-plastics options require separation of the e-plastics into their different polymers to be used by conventional processing options such as injection molding, extruding, and blowmolding. This separation/sorting can be a costly and formidable task. Sorting of e-plastics is often performed manually, but this is cost-prohibitive in the US. The use of automated sorting has been investigated, but requires significant investment in equipment [14].

As a result of these issues, most e-plastics are currently disposed of by landfilling or incineration/ pyrolysis, or shipped overseas for alleged recovery [8,15]. The thermal treatment of e-plastics is of concern because of the potential for the production of emission products, such as brominated dioxins [4,16–19]. The shipment of e-wastes from developed countries to lesser-developed ones has resulted in significant waste disposal and exposure concerns [20–24].

Environmental and Health and Safety (EHS) concerns associated with e-waste recycling exist [4,20,21,23,25–34]. However, informational gaps are present. For example, recent NIOSH Health Hazard Evaluations (HHEs) did not address FRs in workplace air sampling or biological monitoring [25,26]. There is little information on the metal content remaining in e-plastics after separation of the e-metals.

1.3. Analysis of E-Plastics

As noted above, two of the biggest barriers for the recycling of e-plastics are the wide variety of possible polymers in the e-plastics and the potential for FR in these materials. For example,

in the European Union (EU), there is a restriction of 0.1% for BFR concentration in WEEE [13,35,36]. Concentrations of BFR above this value would make it difficult for the e-plastics to be reused or recycled.

The analysis (for sorting purposes) of the different types of polymers can be performed by a wide variety of techniques, of varying complexity and cost. Some examples of techniques that have been used include Fourier transform infrared spectroscopy (FT-IR), non-dispersive infrared spectroscopy (NDIR), Raman spectroscopy, and thermal methods such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC) [37]. Real-time sorting of plastics by type of polymer is being done for regular plastics [14]: however, the equipment often requires a significant upfront investment.

Analysis of BFRs and OPFRs in e-plastics has typically been performed using analytical techniques that involve physical sample preparation by grinding/chopping *etc.*, solvent extraction and cleanup, and extract analysis with gas chromatography-mass spectrometry (GC-MS) [38–42] or liquid chromatography-mass spectrometry (LC-MS) [43–47]. More recently, the use of other methods including X-ray fluorescence (XRF) [48–50], Raman spectroscopy [50], Ion beam analysis (IBA) [51,52], and thermal analytical methods such as thermal desorption GC-MS have been proposed for FR analysis [39,53–55]. XRF and IBA methods analyze for elemental composition, using the Br, Cl, and P levels as a surrogate for the FR itself, *i.e.*, elevated levels of Br, Cl, and/or P would indicate the presence of the FR.

Metals analysis is typically performed using atomic absorption spectroscopy (AAS), inductively coupled plasma and optical emission spectroscopy (ICP-OES), or mass spectrometry (ICP-MS).

The types of analytical methods outlined above are typically associated with expensive instrumentation that require support facilities, and staff with extensive education/training in order for the analyses to be performed reliably. This can result in analytical costs of hundreds to thousands of dollars per sample. This analytical cost often negatively affects the number of samples that can be analyzed in studies. In many cases, the analytical method is excessive for the question being asked; for example, does that e-plastic contain more than 0.1% (1000 ppm) BFR? There are clear opportunities for the introduction of lower-cost and more portable analytical methods for FR in e-plastics that would allow for a faster and less expensive "screening"-type analysis of e-plastics.

1.4. E-Plastics Processing

One potential outlet for e-plastics reuse is compression molding. Currently, e-plastics are available in chopped/ground/shredded granular form with great variance in particle size, color, and polymer composition. Figure 1 is representative of different batches of e-plastic resin generated from an e-waste recycling facility in Illinois. Note the presence of colors and the large, irregular objects that did not completely reduce to granules. Compression molding was one of the first industrial methods for plastics, with equipment dating back 100 years [56]. The basic process consists of heating a thermoset resin, under severe pressure, within a closed mold cavity until the resin cures through a chemical reaction where smaller molecules link forming high-molecular-weight polymeric chains. Under the pressure, the resin also liquefies and flows, taking the shape of the mold cavity, and then hardens into the desired part or product. Once sufficiently cooled and strong, the part is removed from the mold and the cycle is complete although the curing reaction continues while cooling to ambient (room) conditions. Thermoplastics are already fully reacted, thus are shaped by first softening the resin through preheating, within the mold or in an external oven, then using pressure to form the part. Instead of a chemical reaction, a simple phase change takes place as the material again hardens upon cooling. Although compression molding is mostly associated with thermosetting resins, PP is a thermoplastic that is easily and routinely molded by this process.



Figure 1. Typical selection of chopped/ground/shredded e-plastic resin.

This process is suitable for many industrial, commercial, and consumer products from very small appliance knobs to large automobile body panels [56–60]. General product areas are packaging, lighting and electrical, transportation, and appliances. Specific items are electrical wall switch plates and receptacles, circuit breakers, bottle caps, buttons, containers, covers, protective helmets, pump components, gears, brake parts, frames, pulleys, vehicle panels, dishware, and appliance housings, bases, handles, and knobs. Possibilities range from simple geometries to complex three-dimensional shapes, and only very large, longish (pipes, ducts, tubes) or hollow parts are prohibited [56,58].

Compression molding is much less dependent on having a pure, or even known, feed stream composition [56]. Likewise, the process is relatively insensitive to changes in additive (flame retardants being an additive) concentrations. This is due to the fact that the process is fundamentally a heated vise, which applies a closing force upon the two mold halves. The molds are easily separated from the compression-molding machine should there be problems with the molding resin. In other plastic processing techniques, the resin is extruded through the equipment into a mold or die, and material problems may produce significant control problems or even equipment damage. E-plastics are primarily mixed thermoplastics of varying melting points. There can also be thermosets and elastomers present; these cannot be remelted. Therefore, processing conditions such as temperature and pressure cannot be narrowly prescribed. Without sorting, this eliminates the use of e-plastics streams from most plastics processing methods. The simplistic operation and tooling of compression molding makes this process optimal for molding e-plastics. In addition, compression molding equipment is generally less expensive than other plastics processing equipment, so that this processing option is useful for e-plastics' reuse in less developed countries.

There have been experimental studies attempting to mold e-plastics. Lakshmi and Nagan [61] have crushed and ground e-plastics for use as replacement material for a portion of the coarse aggregate in cemented concrete mixtures. Up to 28% of the aggregate was substituted. Strength, durability, and chemical resistance tests demonstrated that e-plastics is a feasible utilization of an otherwise waste material.

In the case of ABS, Arnold, Alston, and Holder [62] compounded granules at 210 °C for four minutes and compression molded them at 210 °C into flat bars for flexural strength testing. Data indicated mostly good strength (above 80% of virgin ABS-molded bars), but some batches exhibited unexpectedly low strength. As much as 50% reduced flex strength was found and attributed to incomplete blending of the resin into a truly homogeneous material and/or voids in the material. The voids were caused by polymer degradation products, primarily from the styrene. Results implied that better mixing prior to molding, along with elimination of the trapped degradation gases, allows for reuse of the ABS.

Balart et al. [63] blended ABS and PC e-plastics in an extruder, at 220 °C, up to 60%, by weight, PC; the blends were injection molded into samples and tensile and impact testing was performed. Tensile strength of blends was slightly lower than that of pure ABS but far below that of pure PC even at 60% PC. Overall, 10%–20% PC represents a reasonable blend with only a small decrease from the 100% ABS level. Some of the decrease was attributed to heat degradation of the butadiene rubber in the ABS. Improved mixing of the two resins into a more homogeneous phase is thought to result in better performance. In another study, ABS and PC e-plastics were washed, then vacuum-oven dried for four hours at 80 °C and 120 °C, respectively, for eventual strength tests [64]. Test coupons were injection molded at 1.0 MPa. Tensile strength of ABS was 16% lower compared with virgin ABS, probably due to degradation of its butadiene phase. Stiffness, as determined through the tensile modulus, decreased about the same level. Flexibility, measured via extension to break, was only half that of virgin resin, and impact strength was lowered by about 35%. Interestingly, tensile strength and modulus of the PC matched its virgin resin. However, its extension to break and impact strength decreased by 25% and 45%, respectively. Then, ABS/PC mixtures were produced using a twin-screw microcompounder at 260 °C and 40 rpm. However, the blends were not as successful, and only further depressed extension as well as tensile and impact strengths from the already lower e-plastics-ABS levels; but tensile modulus values were very near virgin ABS. Some property improvement was found after the blending of coupling agent additives, such as epoxy or nanoclays, into the ABS/PC mixtures, but it should be pointed out that any additives or extra processing contributes to product expense and negates the primary benefit of utilizing e-plastics: its low cost.

1.5. Project Background

The authors received funding from an internal competitive grant program (Research and Artistry) at Northern Illinois University (NIU). The primary objectives for the project were:

- 1. Investigate the feasibility of using e-plastics for compression molding instead of disposal;
- 2. Obtain information on the FR and metals content from samples of e-plastics used for compression molding testing;
- 3. Identify and if possible test, lower cost, simpler, and more portable analytical methods for FR concentration in e-plastics

This paper provides a summary of the preliminary results from this project. Figure 2 contains a schematic of the work.



Figure 2. Schematic representation of work covered in this paper.

2. Results

2.1. Compression Molding of Some Sample E-Plastics

There are currently no established guidelines or data for the processing of e-plastics. Therefore, to increase its value by promoting e-plastics to a usable engineering material, one goal of this study was to assess suitable compression molding conditions. Variables of concern that have been identified are molding temperature, molding pressure, and molding time. Other processing considerations are resin preheating and venting of the mold. Because the generation of e-waste is projected to increase significantly in the future, another objective of this study is to quantitatively characterize some primary mechanical properties; data gathered include mechanical strength.

Figure 3 shows an example of a compression-molding form using the e-plastic shown in Figure 1. The heterogeneous nature of the e-plastic can clearly be seen. To better understand the processability of this material, 15 samples (in groups of three using a three-cavity aluminum mold) were molded and tensile strength tested, yielding a mean tensile strength of 29.3 ± 10.0 MPa. Figure 4 shows this averaged data along with several other selected plastics. The strength is reasonable, compared to other common, commercial plastics, and proves that such heterogeneous e-plastic can be molded without special or extra processing. Along with the measured mean, there exists a large uncertainty (± 10.0 MPa)

in the trials. However, it must be pointed out that the 15 samples originated from six different batches of unknown product of unknown polymeric composition. No attempt was made to systematically sort the e-plastic or vary molding parameters in a design-of-experiments (DOE) fashion. At this time, the goal was to demonstrate that with such a variable and heterogeneous resin could be molded at all. Thus, large uncertainty in the measured strengths was expected.

Although the resin composition in the testing was not known, it is likely that ABS, PS, and/or PC were present. Figure 4 indicates that the material's strength is significantly less than that of these standard plastics or their copolymers and blends. Inspection of individual tensile bars after testing uncovered inclusions of plastic bits that did not soften or melt to fuse with surrounding material along with many internal voids. The inclusions and voids certainly diminish strength. Arnold, Alston, and Holder [38] experienced similar quality problems after processing ABS e-plastic through an extruder prior to compression molding test specimens. Their voids were mostly attributed to styrene degradation gassing and not due to any water evaporation since their pre-dried resin displayed the same behavior.

In future studies, variations in the preheating technique could reduce the level of unmelted bits. Also, a redesign of the mold to facilitate gas and volatiles venting should minimize voidage and similarly improve moldability and strength.



Figure 3. Example compression molding "coaster," Letter ID = L (see Table 1).



Figure 4. Comparative tensile strength of e-plastics from this study. Reference values for LLDPE, HDPE, PP, ABS, PS,g and PC are from Strong [65].

2.2. Preliminary Screening Analysis

Another of the goals for this project was to obtain information on the metals and FR content of e-plastics that were used for the compression molding demonstrations discussed in 2.1. We chose to utilize hand-held XRF as a screening analytical technique, since one of us (Dr. William Mills) has been using this technique since 1992 for EHS issues [66] and instrument availability. The XRF technique is well-suited to the types of materials encountered in the e-plastics. It provides elemental analysis, including for certain instruments, bromine, chlorine, and phosphorus (which can be used as surrogates for the FR). Hand-held XRF offers additional advantages over the typical laboratory XRF analysis in terms of the portability and ease of use, without necessarily any significant reduction in accuracy/precision.

Figures 5 and 6 show some of the samples that were analyzed by hand-held XRF. A total of 27 elements were analyzed using the XRF. Table 1 contains the data generated for a subset of Br, Cl, P, Hg, Pb, Cr, Co, Ni, Cu, which were considered of most interest for this project. Table 2 provides

a summary of the minimum and maximum values for each of these elements. The Table S1 in the supplementary contains the full analysis results for the 27 elements. Additional analytical information is provided in the Materials and Methods section.

3. Discussion

Preliminary molding and testing has shown that e-plastics can be processed with reasonable mechanical strength. Figure 4 compares the measured tensile strength of the e-plastics from this study with some conventional resins [65]. The e-plastics have significantly better strength than linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). However, expectedly, it is weaker than PP, polystyrene (PS), ABS, and PC. Furthermore, it is believed that reducing the voids from gassing during molding is achievable in the future and would recover the e-plastics' strength to near 40 MPa, thus elevating its strength to that of engineering plastics such as ABS and PC. This opens e-plastics to use in many compression-molded products although medical- and food-related ones would be excluded due to the variability in FR content of the e-plastics stream. Products routinely exposed to high temperatures also would not be suitable since the vast majority of e-plastics is thermoplastic with the potential to melt.

Ideally, consumer products with the requirements of moderate strength and durability would benefit from e-plastics. Some projected areas are outdoor stakes, signs, frames, planting containers, fencing, and furniture components. All of these are easily compression molded. From a processing standpoint, even e-plastics with FRs can potentially find reuse. However, the marketplace will most likely find that e-plastics with no or low levels of FRs are acceptable, and all other e-plastics that are either difficult to sort or contain FRs would be landfilled or incinerated for energy production. Additionally, even if the ability to screen and separate e-plastics into batches of homogeneous resins is improved, further research must depend on experimental data as prediction of properties from the composition or content of e-plastics *a priori* is speculative.

There are several things that stand out for the XRF data in the Tables 1 and 2 data. First off, while there is a clear amount of visible heterogeneity in the e-plastics starting material (Figures 1, 3, 5 and 6), there was no immediate or clear way of determining or predicting which e-plastics starting material would be elevated in any of the elemental parameters. There is a large spread on the bromine values with a maximum of approximately 500,000 ppm for (letter ID = D.) Three measurements were made on this item (letter ID, D), two of them were very close to each other, while another was approximately 1/5 of the other two values, but still over 10% by weight (*i.e.*, 100,000 ppm). Based on discussions with the analytical instrument manufacturer (Olympus), this amount of variability at this concentration is not unheard of. All of these results were >100,000 ppm Br, which is much higher than the EU 0.1% total BFR WEEE restriction. For the e-plastics starting material, the black plastic (letter ID, G) had the highest bromine level. None of the e-plastics starting material Br values could account for the high Br values observed in the test bar. In contrast, none of the e-plastics samples contained significant amounts of chlorine or phosphorus (all P measurements were below the limit of detection). The white paper was analyzed without and then with a black marker in order to determine if the black marker had any elevated concentrations. A review of the data in Table 1 does indicate that the paper and black marker were elevated in Cl but not in other elements. In terms of metals, the values seen in the samples were generally quite low, although one e-plastics starting material (letter ID, G) had 259 ppm of lead, one to two orders of magnitude higher than that seen in the rest of the e-plastics.

These results indicate that the separation process being used for e-metals seems to be doing a good job of preventing them showing up in e-plastics. The results also serve to illustrate the heterogeneity issue of e-plastics with regards to FR content, as well as the lack of visual indicators of the FR content and how implementation of a robust screening analysis could help prevent entry into the recycling stream of e-plastics containing FR.



Figure 5. E-plastics samples (A–F) analyzed by hand-held XRF (see Table 1 and Table S1).



Figure 6. E-plastics samples (G–K) analyzed by hand-held XRF (see Table 1 and Table S1).

Material Source	Letter ID (Figures <mark>5</mark> and 6)	Elapsed Time Total	Br	Cl	Р	Hg	Pb	Cr	Со	Ni	Cu
Phenolic Resin—Reference Bar	А	44.13		399	<lod<sup>1</lod<sup>	<lod< td=""><td>9</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>961</td></lod<></td></lod<></td></lod<></td></lod<>	9	<lod< td=""><td><lod< td=""><td><lod< td=""><td>961</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>961</td></lod<></td></lod<>	<lod< td=""><td>961</td></lod<>	961
Phenolic Resin—Reference Bar	А	44.12		420	<lod< td=""><td><lod< td=""><td>6</td><td>11</td><td><lod< td=""><td><lod< td=""><td>983</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>6</td><td>11</td><td><lod< td=""><td><lod< td=""><td>983</td></lod<></td></lod<></td></lod<>	6	11	<lod< td=""><td><lod< td=""><td>983</td></lod<></td></lod<>	<lod< td=""><td>983</td></lod<>	983
e-Plastic Test Bar	B (no photo)	44.68		208	<lod< td=""><td><lod< td=""><td>9</td><td>11</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>9</td><td>11</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	9	11	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Phenolic Resin (powder)	C (no photo)	44.13	43	69	<lod< td=""><td><lod< td=""><td>36</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>2600</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>36</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>2600</td></lod<></td></lod<></td></lod<></td></lod<>	36	<lod< td=""><td><lod< td=""><td><lod< td=""><td>2600</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>2600</td></lod<></td></lod<>	<lod< td=""><td>2600</td></lod<>	2600
e-Plastic—Test Bar	D	43.57	547,244	43	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>170</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>170</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>170</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>170</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>170</td></lod<></td></lod<>	<lod< td=""><td>170</td></lod<>	170
e-Plastic—Test Bar	D	43.65	545,085	36	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>143</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>143</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>143</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>143</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>143</td></lod<></td></lod<>	<lod< td=""><td>143</td></lod<>	143
Blank white paper	Е	45.06	<lod< td=""><td>1705</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>382</td><td><lod< td=""><td><lod< td=""><td>324</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	1705	<lod< td=""><td><lod< td=""><td><lod< td=""><td>382</td><td><lod< td=""><td><lod< td=""><td>324</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>382</td><td><lod< td=""><td><lod< td=""><td>324</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>382</td><td><lod< td=""><td><lod< td=""><td>324</td></lod<></td></lod<></td></lod<>	382	<lod< td=""><td><lod< td=""><td>324</td></lod<></td></lod<>	<lod< td=""><td>324</td></lod<>	324
Blank white paper with Black Marker	F	44.97	<lod< td=""><td>4292</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>575</td><td>2641</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	4292	<lod< td=""><td><lod< td=""><td><lod< td=""><td>575</td><td>2641</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>575</td><td>2641</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>575</td><td>2641</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	575	2641	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Black e-plastic, ground up (Bag-4)	G	43.56	77,904	532	<lod< td=""><td><lod< td=""><td>259</td><td>134</td><td><lod< td=""><td><lod< td=""><td>484</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>259</td><td>134</td><td><lod< td=""><td><lod< td=""><td>484</td></lod<></td></lod<></td></lod<>	259	134	<lod< td=""><td><lod< td=""><td>484</td></lod<></td></lod<>	<lod< td=""><td>484</td></lod<>	484
White e-Plastic, ground up (Bag-1)	Н	43.71	2560	11	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
White e-Plastic , fittings (Bag-2)	Ι	44.56	44	25	<lod< td=""><td><lod< td=""><td>37</td><td>65</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>37</td><td>65</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	37	65	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Purple e-Plastic , fittings (Bag-3)	J	44.42	50	63	<lod< td=""><td><lod< td=""><td>30</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>30</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	30	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
White e-Plastic , fittings (Bag-3)	К	44.18	44	15	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Purple/White e-Plastic, compression mold test	L	43.77	526	21	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Purple/White e-Plastic, Test Bar	M (no photo)	44.38	77	19	<lod< td=""><td><lod< td=""><td>30</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>30</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	30	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
White e-Plastic Test Bar (repeat)	D	44.28	118,564	34	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>28</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>28</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>28</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>28</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>28</td></lod<></td></lod<>	<lod< td=""><td>28</td></lod<>	28

Table 1. Hand-held XRF data for analysis of selected elements in e-plastics.

 1 LOD = limit of detection.

Table 2. Minimum/maximum summary for data in Table 1.

	Br	Cl	Р	Hg	Pb	Cr	Со	Ni	Cu
min	43	11	LOD	LOD	5.6	9.7	2641	LOD	28
max	547,244	4292	LOD	LOD	259	575	2641	LOD	2600

4. Materials and Methods

4.1. Compression Molding

To examine the possibility of compression molding, several small, typical batches of e-plastics were obtained from a northern Illinois recycler (See Figures 5 and 6 and Table 1). The white e-plastic in Bags 1 and 2 are believed to have been produced from grinding of the "fittings" in Bags 2 and 3. Their exact compositions were unknown but ABS and PC are thought to be the dominant plastics. By varying molding temperature and pressure with the inclusion of preheat, visually reasonable test bars were produced with this material. The optimal conditions included softening the charge with 30 min of preheat at 204 $^{\circ}$ C, followed by a molding pressure of 17.2 MPa at 204 $^{\circ}$ C for 4 min. A 7075-T651 aluminum three-cavity mold was utilized. It has a mass of 5.8 kg and, when closed, measures 191 mm in length, 152 mm in width, and 70 mm in height. The molder was a commercial, 267 kN electric/hydraulic unit (Model AutoFour/30-D, Carver Inc., Wabash, IN, USA [67]) with $305 \text{ mm} \times 305 \text{ mm}$ heated platforms. The tensile bars are the typical ASTM [68] "dog-bone" shaped—165.1 mm long, with width and thickness in the narrow (*i.e.*, break) region measuring 12.7 mm and 3.2 mm, respectively. Consistent samples were produced, as demonstrated by their uniform thickness, even when molding up to three at once. Using a commercial, 24.5-kN tensile tester (Model EZ 50, Lloyd Instruments Ltd., Hampshire, UK [69]) according to ASTM D638-14 [68] each tensile bar was pulled until complete break with this corresponding to the ultimate, and maximum, tensile strength (UTS) of the material. Tensile pulling speed was 5 mm/min for all samples.

4.2. Hand-Held XRF Analysis

An Olympus Delta Professional hand-held XRF [70] (Olympus, Newton, MA, USA) was used for XRF analysis. This instrument was calibrated by the service center prior to use [71]. Samples were analyzed on a "as is" basis. The soil mode was utilized for all analyses. For each sample three readings were obtained of approximately 15 seconds each (*i.e.*, total analysis time of approximately 45 seconds for each result) and the average value was calculated, along with a standard deviation. Tables 1 and 2 contain selected XRF data. The complete data set produced is contained in Table S1 of the supplementary file.

5. Future Research and Conclusions

The preliminary data produced for the compression molding is promising and adds to the available data set for e-plastics. However, the two biggest obstacles to the reuse/recycling of e-plastics remain the heterogeneity in the types of polymers and the heterogeneity in terms of the flame retardant concentrations. Future work is being undertaken at NIU that will address both of these issues.

For the FR analysis in e-plastics, the hand-held XRF appears to be very promising, considering cost, ease-of-use, portability, performance, and sample throughput. Additional work is planned with hand-held XRF using both the Olympus as well as those from other instrument manufacturers. This work will include the evaluation of options such as a built-in camera, different data processing, and source configurations. The XRF, while an excellent screening tool, does not provide quantitative information for the FR, as it is only measuring the elemental bromine, chlorine, or phosphorus. Therefore, additional work is planned to compare the XRF with other FR screening and quantitative analytical techniques. These planned techniques include Handheld XRF [66] [72,73], Ion beam analysis/spectrometry (IBS/IBA) [51,52,74], High resolution 2D-gas chromatography-time-of-flight mass spectrometry(HRGCxGC-TOFMS) [75], and Thermal desorption-time-of-flight mass spectrometry (TD-HRGC-TOFMS) [54]. This additional work is expected to generate information which can be used to address issues related to ease-of-use, data comparability, and potential cost of analysis for some simpler analytical methods.

Finally, we believe that having readily available methods of identifying the class (or type) of polymers in the e-plastics is still an important need to address to allow for more recycling/reuse

of e-plastics. While automatic sorting technologies are used in commercial plastics recycling, there is a need for techniques that may predict compression molding performance and, are lower cost and/or more portable. Future work therefore will include the evaluation and use of polymer screening techniques such as infrared technologies (FT-IR, NDIR) or thermal analysis (differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) *etc.*) to more thoroughly characterize the e-plastics mixtures tested for compression molding.

Supplementary Materials: The following are available online at www.mdpi.com/2078-1547/7/1/13/s1. Table S1: Full Data Set for Handheld XRF Analysis.

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Author Contributions: William Mills and Robert A. Tatara both conceived, planned, conducted the experiments, reviewed and analyzed the data, and wrote the paper jointly.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ABS	acrylonitrile butadiene styrene
BFR	Brominated flame retardante-wa(s)
DOE	Design of Experiments
DSC	Differential scanning calorimetry
e-metals	Metals derived from e-waste
e-plastics	Plastics derived from e-waste
EÛ	European Union
e-waste	Electronic waste (e-waste), see also WEE
EHS	Environmental and Health and Safety
FR	Flame retardant(s)
FT-IR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
HDPE	high-density polyethylene
HIPS	high impact polystyrene
HHEs	NIOSH Health Hazard Evaluations
HRGCxGC-TOFMS	Two-dimensional high-resolution gas, tomography-time-of-flight mass spectrometry
IBA	ion beam analysis, see also IBS
IBS	ion beam spectrometry, see also IBA
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
LC-MS	Liquid chromatography-mass spectrometry
LLDPE	linear low-density polyethylene
LOD	limit of detection
NDIR	non-dispersive infrared spectroscopy
NIOSH	National Institute of Occupational Safety and Health
NIU	Northern Illinois University
OPFR	Organophosphorus flame retardant(s)
PBDE	polybrominated diphenyl ethers
PC	Polycarbonate
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
TD-GC-MS	Thermal desorption-gas chromatography-mass spectrometry
TD-HRGC-TOFMS	Thermal desorption-high-resolution gas chromatography-time-of-flight
	mass spectrometry
TGA	Thermogravimetric analysis
US	United States
USEPA	United States Environmental Protection Agency
UTS	Ultimate tensile strength
WEEE	Waste Electrical and Electronic Equipment
XRF	X-ray fluorescence

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