

POLYPROPYLENE RECOVERED FROM SHREDDED END-OF-LIFE DURABLE GOODS

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Abstract

Our industry leading separation technology enables us to recover polyolefins and styrenic plastics from complex mixed streams such as shredded end-of-life vehicles and waste electrical and electronics equipment. Plastic flakes recovered using our process are compounded and sold as pellets suitable for use in injection molding and extrusion applications. This paper looks at the challenges and benefits of recovering polypropylene and modifying its properties for use in various injection molded parts in the horticultural, construction, packaging and automotive industries.

Introduction

The volume of plastic produced globally in 2014 was 311 million metric tons [1]. The distribution of plastics demand by segment in Europe from the same study is shown in Figure 1.

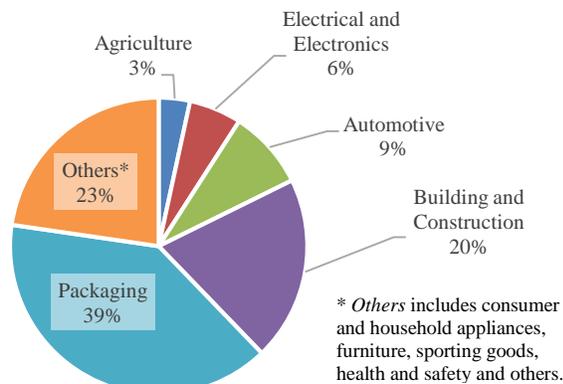


Figure 1. Distribution of European plastics demand by segment in 2014 [1]

Studies have shown that recycling is the preferred environmental option for plastics at the end-of-life [2,3], but the fraction of plastics recycled was only 29.7% in Europe in 2014. Plastics from packaging were the most recycled, with national recycling rates mostly in the range of 25-50%. This suggests that plastics from durable goods such as automobiles and electrical and electronics equipment (E&EE) were recycled at rates well below 30%.

In the US, recycling rates of plastics tend to be even lower. The rate of plastic recycled from municipal solid waste (MSW) was only 9.5% in 2014 [4]. Recycling rates from durable goods in MSW was even lower, at 7.5%.

Many of the plastics in durable goods are highly engineered to meet the long-term performance requirements of these products, so it would be beneficial if these plastics could be recycled at higher rates. Such products can often be used in less demanding applications that might still typically use virgin plastics, but in some cases these plastics can be used in durable goods in applications similar to their original use. Such efforts are also a key part of the Circular Economy [5], as much of the recycled plastic currently used in automobiles is from sources other than durable goods [6].

When automobiles reach the end of their life, parts are often removed for re-use (i.e. replacement parts for running automobiles) or for recycling (e.g. catalytic converters and some larger plastic items such as bumpers). Automobiles also undergo a decontamination step which includes removal of fluids, batteries and tires. After the decontamination step, automobiles are compacted and then shredded (often along with other metal-containing items such as large home appliances and demolition debris along with end-of-life vehicles [7]) to enable recycling of the remaining materials in the automobile. The material remaining after most of the metal is recovered is known as automobile shredder residue (ASR). ASR contains the majority of the plastics from end-of-life vehicles, though it is most often sent to landfill in the US. The recycling industry expects that 1.6 million metric tons of plastic could be recovered annually from ASR in the US [8].

The method of handling waste electrical and electronics equipment (WEEE) depends on the type of product and where the product is recycled. Some handling of WEEE is necessary in order to remove hazardous components such as cathode ray tubes or batteries. Some recyclers take the hand dismantling further and end up recovering large pieces of plastics that can be baled and sold to plastic recyclers [9]. Other recyclers shred the WEEE (after removal of hazardous components) and recover the metals using methods similar to those used by recyclers of automobiles. The remaining material after most of the metal is recovered, which we refer to as electronics shredder residue (ESR), may be further processed by plastic recyclers with automated sorting equipment. The latter method of recycling plastics from WEEE is most common in Europe, whereas both approaches are practiced in the US [9].

European Directives covering end-of-life vehicles (ELV) and WEEE in fact provide targets for recycling of these end-of-life products [10, 11]. The recycling targets are based on the entire weight of these products. The targets can only be partially achieved through the recycling of metals, so some portion of the plastics must also be recycled.

In response to these targets for plastic recycling, a number of recyclers in Europe have been recovering plastics-rich streams for recycling for a number of years. In previous papers [12,13,14], we have described our plastic recycling facilities that recover plastics from upgraded ASR (in the United Kingdom) and ESR (in Austria).

Plastics from ELVs include polypropylene (PP), high density polyethylene (HDPE), acrylonitrile-butadiene-styrene (ABS), polyamides (PA), polycarbonate (PC), blends of PC with ABS (PC/ABS) and many others [15,16]. Other plastics, such as high impact polystyrene (HIPS), are also present in shredder residue because of the shredding of large appliances such as refrigerators.

Plastics from WEEE include acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS), polypropylene (PP), polyamides (PA), polycarbonate (PC), blends of PC with ABS (PC/ABS), flame retardants grades of ABS and HIPS (ABS-FR and HIPS-FR), mineral and glass filled grades of PP, polyvinyl chloride (PVC), polyoxymethylene (POM) and many others [13].

PP is the largest volume plastic product present in ASR. It is also found in ESR, but in a smaller amount. In this paper, we first summarize the feed materials and separation process used to recover PP from these complex streams. Next we discuss the composition and properties of the PP products. We then discuss some of the limitations and potential improvements to these products. Finally, we give some case studies where the material has been successfully in place of virgin PP in demanding applications.

Compositions of ASR and ESR

Typical ASR only contains a small portion of plastic, so further processing is required to make this stream more interesting economically for plastic recycling. The mixture can be upgraded using processes available in the recycling industry. Such an upgraded ASR mixture is what is fed to MBA Polymers' facility in the UK [14].

Table 1 summarizes typical compositions of mixtures fed to MBA Polymers' facilities in the UK (upgraded ASR) and Austria (European ESR).

Table 1. Example compositions of upgraded ASR and European ESR as fed to the MBA Polymers process

Material	Upgraded ASR	European ESR
“Target Plastics”	77%*	61%‡
Other plastics	7%	25%
Rubber	6%	3%
Wood	5%	3%
foam, textiles, paper and film	3%	1%
Other materials	0%	1%
wires and metal	1%	5%
“fines” (<3 mm)	1%	1%

* PP, ABS, 20% filled PP, HIPS and HDPE

‡ ABS, HIPS, PP, PC/ABS

Process to Recover Plastics from Shredded End-of-Life Durable Goods

MBA Polymers has considerable experience and technical know-how for processing streams of plastics from durable goods such as ESR or upgraded ASR. Some of the technologies employed to create high value products from these streams are covered in more detail in our patents [17].

The MBA Polymers process to recover plastic products from ESR is summarized in Figure 2. The process for recovering plastics from ASR is similar, though PC/ABS is not currently recovered, and both HDPE and PP (20% mineral filled) are recovered as separate products.

Initial steps of the process include size reduction and processes to removal non-plastics such as metal (mostly from wires), wood, rubber and foam. Next, the plastic-enriched stream is separated into streams of plastic “families”. These plastic “families” each contain significant amounts of one or more major plastic types as well as minor amounts of other plastics, rubber and wood. The next steps include the removal of the majority of the remaining non-plastics (i.e. rubber and wood) and purification of the plastics by type. The purified flakes are then blended in large blending silos prior to compounding.

Figure 3 is a photograph of a mixture of PP flakes recovered from upgraded ASR using the MBA Polymers separation processes.

Product flakes are compounded using a twin screw extruder. This step includes the addition of additives (usually small amounts of antioxidant, colorant, impact modifier and/or others as required), vacuum de-volatilization and melt filtration.

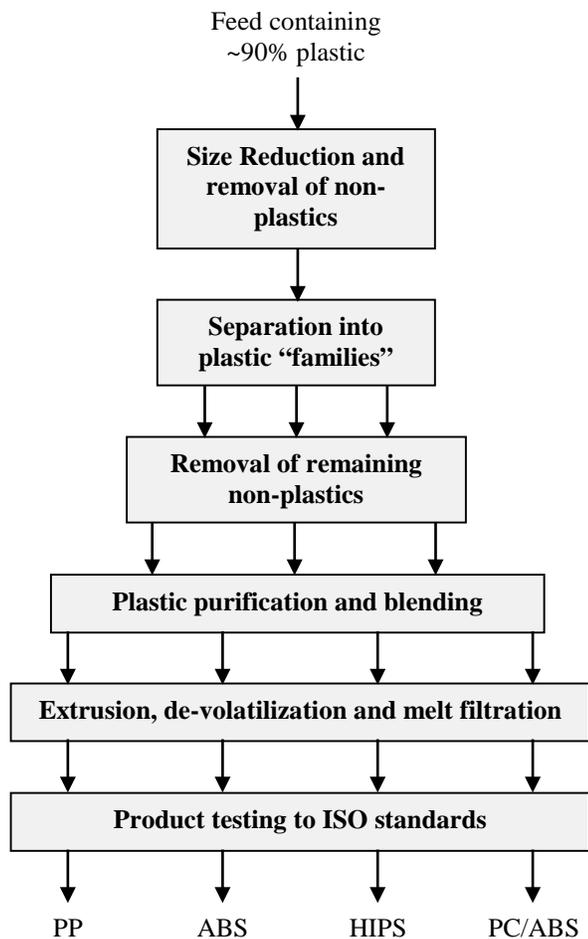


Figure 2. Process for recovering plastics from ESR



Figure 3. PP flakes recovered from upgraded ASR

The final products are tested using ISO standards to ensure product quality. These tests include measurements of moisture, density, melt flow rate (ISO 1133), tensile strength (ISO 527), notched Izod impact strength (ISO 180) and flexural modulus (ISO 178).



Figure 4. PP pellets from upgraded ASR after compounding flakes with small amounts of additives

Polypropylene Products from ASR and ESR

PP Flake Mixtures Prior to Compounding

The purified PP flake mixture recovered from upgraded ASR is a complex mixture that includes various grades of impact copolymer PP from automotive sources (which is itself a multi-phase mix of isotactic PP, ethylene-propylene copolymer, ethylene-propylene-diene copolymer and others [18,19,20]), copolymer PP grades from E&EE and large appliances, mineral filled PP grades and HDPE.

The purified PP flake mixture recovered from ESR is a slightly less complex mixture that includes mostly copolymer PP grades from E&EE.

PP Properties and Applications

Several standard grades are produced by compounding the purified PP flakes with small amounts (typically <2%) of additives. Table 2 summarizes the typical properties of three of the most commonly produced grades.

PP 2126 is the base product from upgraded ASR. PP flakes are compounded with a small amount of antioxidant along with impact modifiers. PP 2126 is suitable for a number of applications requiring good toughness. Specific examples of parts manufactured using PP 2126 include injection molded pallets and plant trays thermoformed from extruded sheet. The fairly low melt flow rate (MFR) prevents its use in some applications (e.g. products with very thin walls), though, so higher flow grades are also available.

PP 2172 is produced from the same flake material as PP 2126, but the MFR is modified to satisfy customers requiring better flowing PP. PP 2172 loses some of its mechanical properties (especially impact strength) due to the additives required to reduce the PP molecular weight,

but it still has sufficiently good mechanical properties for a number of applications in the horticultural, construction and packaging industries. Specific examples include plant pots, waste baskets, storage boxes and crates.

PP 2131 is produced from flake recovered from ESR. This material has a lower impact strength than PP 2126, but has a much higher flexural modulus. Specific applications of this grade include several in new automobiles, including a cable tray used in a luxury automobile.

Table 2. Typical properties of PP products recovered from upgraded shredder residue at MBA Polymers UK

Property	Units	PP 2126	PP 2172	PP 2131
MFR (230/2.16)	g/10 min	7	25	8
Izod impact, notched	kJ/m ²	20	9	6
Tensile strength at yield	MPa	19	18	24
Flexural Modulus	MPa	850	850	1500

Chemical and Thermal Characterization

We have characterized the PP 2126 and PP 2131 products using FTIR. Figure 5 compares the FTIR spectra of PP 2126 and PP 2131 with a virgin copolymer PP. We note that the absorptions overlap reasonably well, though we do note a significant absorption near 1050 cm⁻¹ due to the presence of ~4% talc (based on TGA measurements) in the PP 2126 sample.

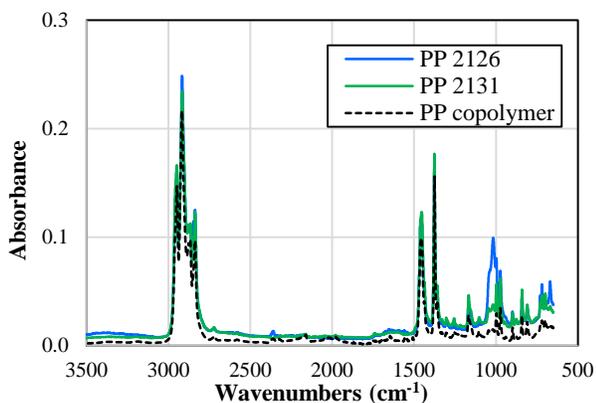


Figure 5. FTIR spectrum of standard PP products from upgraded ASR (PP 2126) and ESR (PP 2131) compared with a virgin PP copolymer

We have also characterized PP 2126 and PP 2131 using differential scanning calorimetry (DSC). Figure 6 shows a DSC thermogram (2nd heat at 10°C/min) with melting endotherms for PE (peak at 127°C) and for PP (peak at 164 or 165°C). The thermograms are typical of PP

copolymers, though there is a higher ratio of crystalline PE to crystalline PP in PP 2126 (as indicated by the higher ratio of PE to PP melting enthalpies). This is consistent with PP 2126 being an impact copolymer grade with a higher impact and lower flexural modulus than PP 2131.

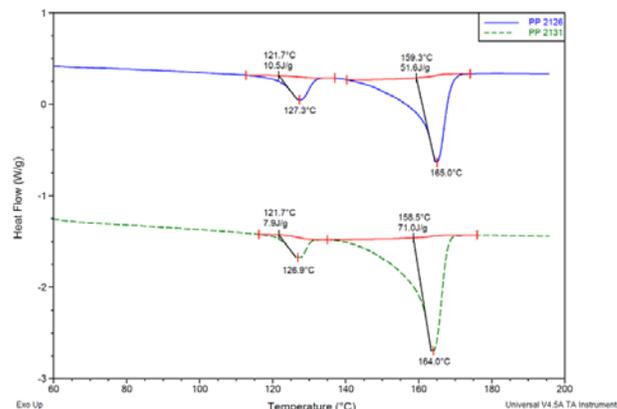


Figure 6. DSC thermogram for PP 2126 and PP 2131 (2nd heat at 10°C/min) showing melting for PE and PP phases

Product Limitations

PP products recovered from ASR and ESR do suffer from a number of limitations that make their use in some applications more challenging. The limitations include:

- Residual semi-volatile organic compounds (SVOCs) and associated odors
- Low flexural modulus (for grades from ASR)
- Color limitations
- Contamination from non-melt particles
- Consistency of properties
- Substances of concern

While PP grades recovered from ASR and ESR can be used in a wide variety of applications, the presence of SVOCs (and associated odors) provides a challenge to their use in demanding applications such as automobile interiors. We are continuing to investigate cost-effective methods to reduce SVOCs and odors for plastics from ASR [21], though we have made significant progress with PP 2131 from ESR (see the Product Development Case Study on “PP from ESR used in Automotive Cable Tray” later in this paper).

The flexural modulus of the PP grades recovered from ASR is approximately 10-20% lower than some virgin high impact PP grades with which we are competing. While this is not an issue for many applications, it can be problematic when the part is under a flexural load and where flexural creep might occur. Later in this paper, we discuss an example of how the flexural modulus and flexural creep resistance were improved for a particular application (see

the Product Development Case Study on “Gray PP with High Flow for Paint Cans”).

The color of the PP products is limited by the existing carbon black, TiO₂ and other pigments present in the PP found in ASR or ESR (see Figure 3). Therefore, the “natural” colors of the PP products are a light black (if from ASR) and a medium dark (if from ESR). Commercially available color sorting equipment can be used to separate the flake mixture into lighter and darker colored mixtures, but this results in added costs and diminished available volumes of any given product. Adding carbon black or TiO₂ pigments in the compounding step also allows for some adjustment of the color, though it is very difficult to achieve deep black colors when TiO₂ is present even in small amounts. Achieving very light gray is difficult even with color sorting and it is not possible to achieve meaningful volumes of white product from either ASR or ESR. Colors other than gray or black are possible by adding colorants to the light colored fraction after color sorting, but these products tend to be expensive and large volumes are not possible.

Although there are a number of process steps to remove non-melts (e.g. wood and rubber) from both flakes and the melt, the PP products contain traces of particulate contamination. These particulates are mostly smaller than approximately 100 microns in size, and have little effect on most mechanical properties, but they are large enough to be visible when extruded or injection molded parts are examined closely.

Even though the flake composition and additive loadings are well controlled in the production of PP products from ASR and ESR, we have observed that the mechanical properties can vary measurably from batch to batch. In a paper presented at ANTEC 2016, we discussed this variation in PP 2126 (up to about $\pm 20\%$ variation in notched Izod) and presented an approach to rapidly measure the mechanical properties of the PP product by statistical analysis of FTIR spectra [22].

PP products from ASR and ESR also contain trace amounts of “legacy” substances of concern such as heavy metals and flame retardants because many of the used vehicles and E&EE comprising the ASR and ESR were manufactured prior to restrictions on these substances. Because of these “legacy” substances of concern, we DO NOT recommend our products for toys, for medical applications or for applications that involve food contact or human oral contact. We do note, however, that our products are RoHS [23] and REACH [24]-compliant and substances of concern are below limits established in the candidate list of substances of very high concern (SVHC) published by the European Chemicals Agency (ECHA) [25] and in the Global Automotive Declarable Substance List (GADSL) [26].

Product Development Case Studies

Gray PP with high flow for paint cans

A manufacturer of plastic paint cans required a dark gray post-consumer recycled PP with a melt flow rate of approximately 20 g/10 min (or higher), sufficient toughness to withstand various impact tests, shrinkage similar to virgin PP grades used to make lids for the can, and sufficient creep resistance to withstand a test designed to mimic the stacking of filled paint cans on a pallet. The recycled PP is to be added at 25% into virgin PP that the molder has historically used for the cans.

Initially, the molder tested PP 2172 at a 25% loading in virgin PP. The molder found that the compound passed tests for shrinkage and impact, but failed the creep test.

As the creep test resulted in failure due to excessive flexing of the walls of the can, we developed a formulation with a 5-10% higher flexural modulus that would better resist any deflection during the test. The formulation included a TiO₂ masterbatch to slightly lighten the color to the desired medium dark gray, a peroxide to control the MFR, an antioxidant to stabilize the end product against oxidation during processing and use, and an additive to increase the flexural modulus by approximately 5-10%. The newly formulated product easily passed the creep (and other) tests performed by the molder.

PP from ESR used in Automotive Cable Tray

A tier 1 molder for a luxury automobile manufacturer required a recycled PP material for use in a cable tray. MBA Polymers facility in Austria sampled their PP 2131 product for the application.

In order to pass the required tests for thermal stability, the product was specially formulated with heat stabilizers.

In order to meet stringent requirements for odors and emissions of volatile organic compounds in this automotive interior application (e.g. VDA 270 and VDA 278), the PP 2131 product was compounded carefully while ensuring optimal vacuum de-volatilization.

Conclusions

PP products recovered from shredded end-of-life durable goods and further compounded into pellets by MBA Polymers are useful for a number of injection molding applications. Though some limitations in properties remain, we continue to improve the products to expand the range of end products in which they can be used. These advancements have resulted in the use of at least one of the PP products as a replacement for virgin PP in an automotive interior application.

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