[CASE STUDY]

A Consolidated Approach for Analytical Testing of Recycled Industrial Plastics

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The plastic industry and commercial enterprises utilizing plastic to manufacture various products such as automotive components, are facing the challenge of finding solutions for circular economy and climate protection. A key solution to lower CO_2 emissions in the transport sector is to replace metal with far lighter high-performance polymers. This route would be further improved through the re-use and/or recycling of plastic waste into new and useful products without compromising on quality or safety.

Recycling or re-using polymeric-based materials strongly depends on the polymer type. Thermoplastic polymers, such as polyamide (PA) commonly known as Nylon, are widely used in the manufacturing of a variety of consumers or industrial products. This is due to their properties such as low density, wear resistance, coefficient of friction and chemical resistance in contact with oils, and impact properties etc. These properties make PA polymers an ideal material for metal replacement in the automotive industry. The use of recycled PA in automotive applications has significant environmental advantages, as it can prevent the generation of greenhouse gases equivalent to those produced by 400,000 cars. [1] The thermoplastic nature of polyamides allows them to melt, making them suitable to be shaped into different products by extrusion or injection molding but also, recycled using the same methods.

Thermoplastic properties of a polymer tend to degrade during use and especially during the recycling processes. For any products that use recycled plastic the properties and structure would have to be analysed, especially if the intention is to use these products in higher value parts such as a car gear box component. Additionally, testing the structure and properties of recycled parts is also important to determine the maximum recycling cycles and the need for addition of virgin materials and additives. Currently there are no clearly defined binding targets for post-consumer thermoplastics in new cars but European Recycling Industries' Confederation (EuRIC) suggests targets of recycled plastics in new car components of 25% by 2025, 30% by 2030, and 35% by 2035.[2] Consequently, in the absence of regulatory directives there is no clarity on what analytical methods are suitable to test recycled industrial parts and assess the suitability and safety aspects.

Recently, a comprehensive literature review looking at the application of recycled plastics in safety-related components was reported [3]. When recycling such parts, it is critical to assess both mechanical properties and chemical properties of the finished product to ensure that performance is not affected. However, due to the uncertainties of the material properties in mechanical recycling, there are limited studies on the use of regranulates in safety-relevant components. As a result, the literature recommends that no more than 25% recyclate should be used, especially for technical parts. A proportion of less than 5%, on the other hand, is considered tolerable and can be done without further testing of the properties.

This case study describes a combined analytical approach to test the structure and properties of polyamide gears processed by extrusion/injection molding of virgin or recycled (regrind) pellets. The workflow described is aimed at analyzing the potential differences of the virgin and recycled pellets and gears.

Thyssenkrupp aims to implement a classic post-industrial recycling workflow as illustrated in figure 1. In addition to the virgin polymer pellets, a high percentage of shredded polymer is added to the hopper of the molding machine. Thus, allowing a zero-waste production line for safety critical gear systems

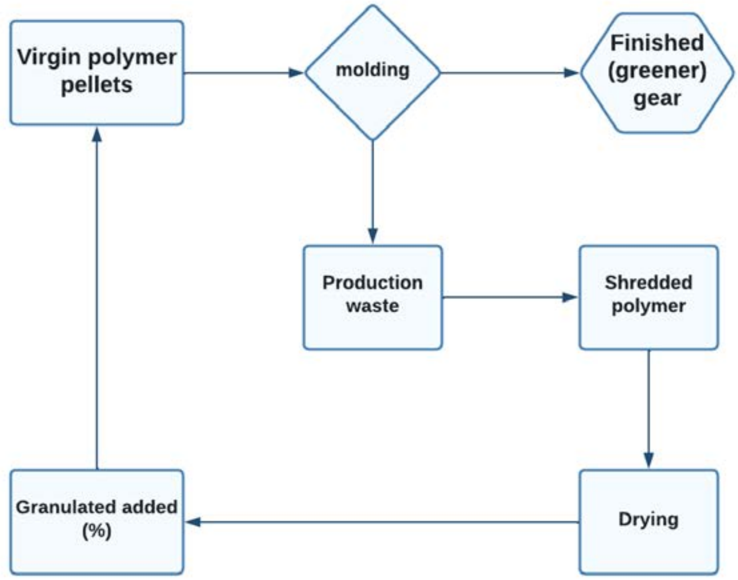

Figure 1. Workflow describing the recycling of scrap PA from injection molded gear parts.

MATERIALS TESTED

A special development material, PrestaMID™, which consists of 95% high-molecular-weight polyamide, was used to investigate recyclability. The aim of this work was to assess the influence of increased amounts of regrind material on product performance and quality and evaluate the possible use of post-industrial recycled polyamide in the worm gear of the steering gear. In post-industrial recycling (PIR), production waste is added to the raw material. In the test series, the regrind is fed back into the process and its proportion is varied.

Chemical-physical and mechanical analyses were carried out to characterize the effects of the regrind on the material and component properties. Molecular level assessment with size exclusion chromatography, material properties testing with thermal analytical instrumentation and an in-depth analysis of recycled plastic pellets and gears using high resolution time of flight mass spectrometry were performed *(Figure 2).*

The long-term load-bearing capacity of the component under dynamic loading is to be tested since this is critical for its use in the steering system of the automobile. This holistic approach should enable an evaluation of polymer recycling for the use of pellets in safety-relevant components using the example of the worm wheel.

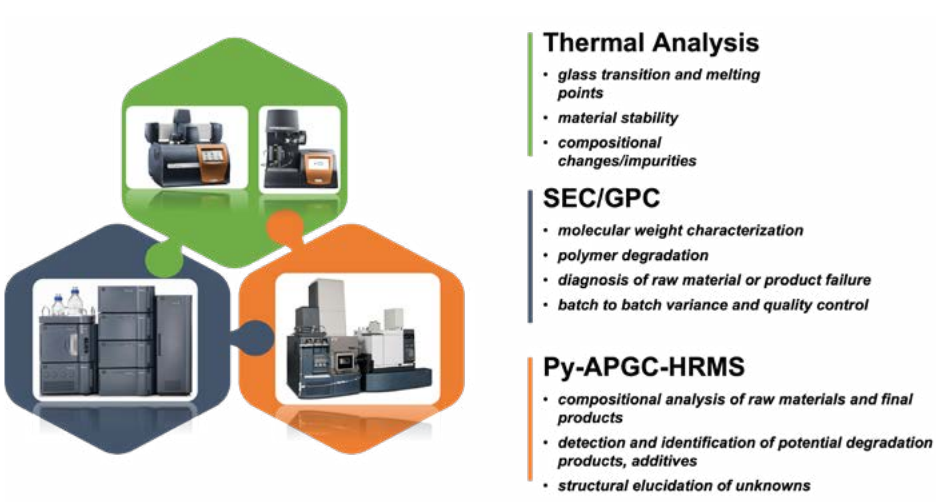

Figure 2. The analytical workflow employed to test the structures and properties of virgin and recycled PA pellets and final gear parts using thermal analysis, size exclusion chromatography/gel permeation chromatography (SEC/GPC) and pyrolysis gas chromatography coupled to high resolution mass spectrometry (py-APGC-HRMS) coupled to high resolution time of flight mass spectrometry

THERMAL ANALYSIS

The recycling and further use of plastics is becoming increasingly important in the context of the sustainability discussion. The aim is to reuse an input of plastic materials as regranulates for production and at the same time to return them to the circular economy. To be able to diversify the plastics and the additives received and to characterize their properties, comprehensive thermal-mechanical analysis techniques are needed.

Thermal analysis methods such as thermogravimetric analyzer (TGA) or differential scanning calorimetry (DSC) can reveal whether the plastic product meets the expected specifications once it has been through the manufacturing process. This approach can be applied to test the unrecycled or recycled raw materials (pellets) as well as the final products (following injection molding, addition of scrap material, additives, virgin material mixed with regrind) to ensure that the material properties are as expected.

"Selective, fast and robust analytics for the regranulated plastics is a prerequisite for ensuring the quality of the materials used. Thermal analysis is excellent for this. With relatively little effort, information about the melting and crystallization behavior of the regranulated materials as well as the temperature range relevant for decomposition and/or the heat of decomposition to be expected can be obtained by heating with a suitable temperature programme".

Agnieszka Kalinowska, Senior Specialist Polymer Materials, Team Leader System Analysis & Polymers at R&D at thyssenkrupp Presta AG

THERMOGRAVIMETRIC ANALYSIS

The mass loss and mass loss rate as function of temperature for the samples in compared in Figure 3. Samples show similar decomposition behavior with the 100% gear and pellet showing less stability. The 100% gear reaches maximum mass loss rate at a temperature approximately 20 °C lower than the other samples, the 100% pellet approximately 10 °C lower *(Table 1)*. The other samples show a slight decrease in temperature at maximum mass loss rate as a function of added regrind PA.

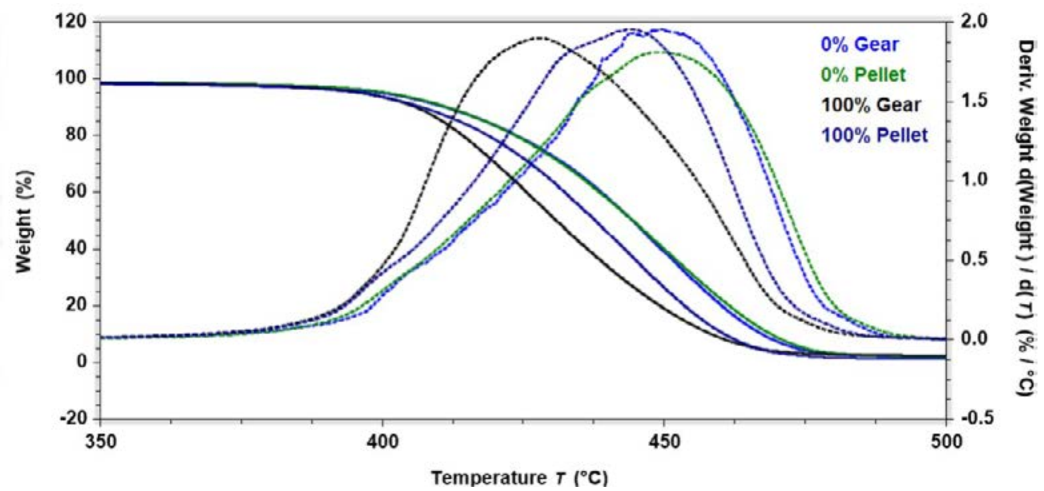

Figure 3. TGA comparison of mass loss and mass loss rate as function of temperature

Table 1. Temperature at maximum decomposition rate

Sample	Temperature at Maximum Decomposition Rate (°C)
0% Gear	449.3
0% Pellet	449.2
100% Gear	427.8
100% Pellet	434.4 / 444.1

DIFFERENTIAL SCANNING CALORIMETRY

The degree of crystallization of gear samples with increased amounts of regrind was also tested with the DSC, a rapid method for determining polymer crystallinity based on the heat required to melt the polymer. The results clearly indicate that all samples are almost identical in terms of melting temperatures (Tm) and crystallinity, with 100% recycled gears having slightly higher crystallization value *(Table 2).*

Table 2. Melting temperatures and crystallization of gear samples containing increased amounts of regrind material

Gear samples (percentage recyclate)	*Tm* (ºC)	Degree of crystallization (%)
0%	256.88	22.0
10%	260.62	23.2
20%	257.55	22.7
36%	256.57	23.5
100%	261.61	25.6

The glass transition region in the first heat is shown in *Figure 4*. Each of the samples shows evidence of enthalpic recovery (due to enthalpic relaxation of the amorphous phase) which appears to correlate with added regrind. Enthalpic relaxation is correlated with brittle fracture so this may be a potential problem.

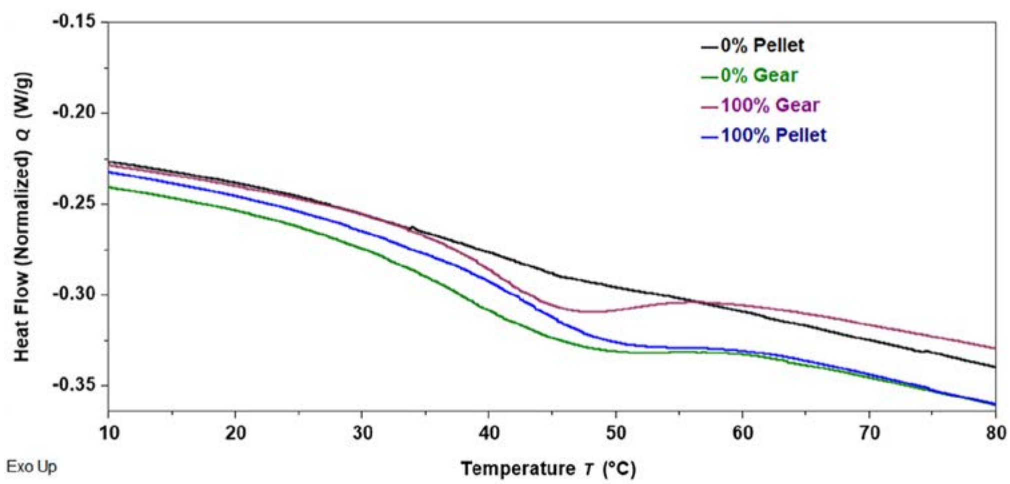

Figure 4. First heat glass transition region showing enthalpic recovery

To investigate this, modulated DSC (MDSC) was used to separate the glass transition which is a step change in heat capacity from the enthalpic recovery endotherm which results from the kinetic enthalpic relaxation process. *Figure 5* shows the result of the MDSC experiment for the 100% recycled gear. The enthalpic recovery is isolated in the non-reversing heat flow signal and can be integrated. *Table 3* summarizes the energy associated with enthalpic relaxation after correction for the frequency effect. [4] There appears to be a correlation between the enthalpic recovery and the mass percent of added regrind *(Figure 5)*, but further study is warranted. A designed experiment is needed to ensure that each sample has the same thermal history and aging time and temperature.

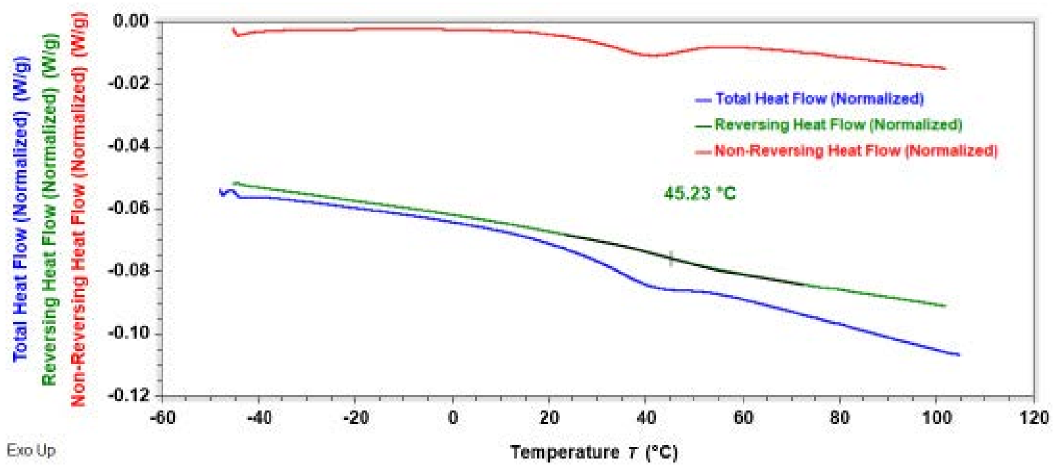

Figure 5. MDSC data for 100% recycled gear

Table 3. Enthalpic recovery energy data for sample set

Sample	Integral 1st Heat	Integral 2nd Heat	Corrected Integral
	J/g	*J/g*	*J/g*
0% Pellet	-1.14	-0.20	-0.94
0% Gear	-2.49	-0.74	-1.75
100% Gear	-1.67	-0.20	-1.46
100% Pellet	-3.61	-0.24	-3.37

SIZE-EXCLUSION CHROMATOGRAPHY (SEC)/GEL PERMEATION CHROMATOGRAPHY (GPC)

SEC/GPC can be applied to investigate the quality of materials containing recycled portions. Recycled raw material is only accepted when it offers a performance similar to virgin materials. However, polymeric chains could degrade each time they are processed and consequently, the molar mass distribution, which is important for the properties of the final product, could be different for regrind material.

Due to the chemical resistance of polyamides, such as Nylon 6,6, dissolving the polymer in an organic solvent for analysis using GPC is challenging. Many manufacturers use high temperature GPC (>100 °C) to determine the molecular weight distribution of these nylon polymers, and the analysis often uses ortho dichlorobenzene (ODCB), trichlorobenzene (TCB), m-cresol or N-methyl pyrrolidone (NMP) as the mobile phase with traditional styrene divinylbenzene (SDVB) GPC columns. [5]

The gear sample molecular weight distribution data were obtained with an alternative GPC analysis using hexafluoro isopropanol (HFIP) as a mobile phase and an advanced polymer chromatography (APC)™ system (Figure 6 and Table 4). The overlay of two gear sample GPC peaks is displayed in figure six using a photodiode array (PDA) detector. Although the peak overlay does not appear to be a large difference, the calculated molecular weight is a 24% difference. The gear containing zero percent recycled nylon has a peak maximum

(MP) molecular weight of 127 KiloDalton (KDa) compared to 97 KDa for the gear with 100 percent recycled polymer. The difference in the peak values is also seen in the weight average (Mw), number average (Mn), z-average, and polydispersity index (PDI) in table 4. Each change in these various values can affect the properties of the polymer strength, melt flow, and flexibility.

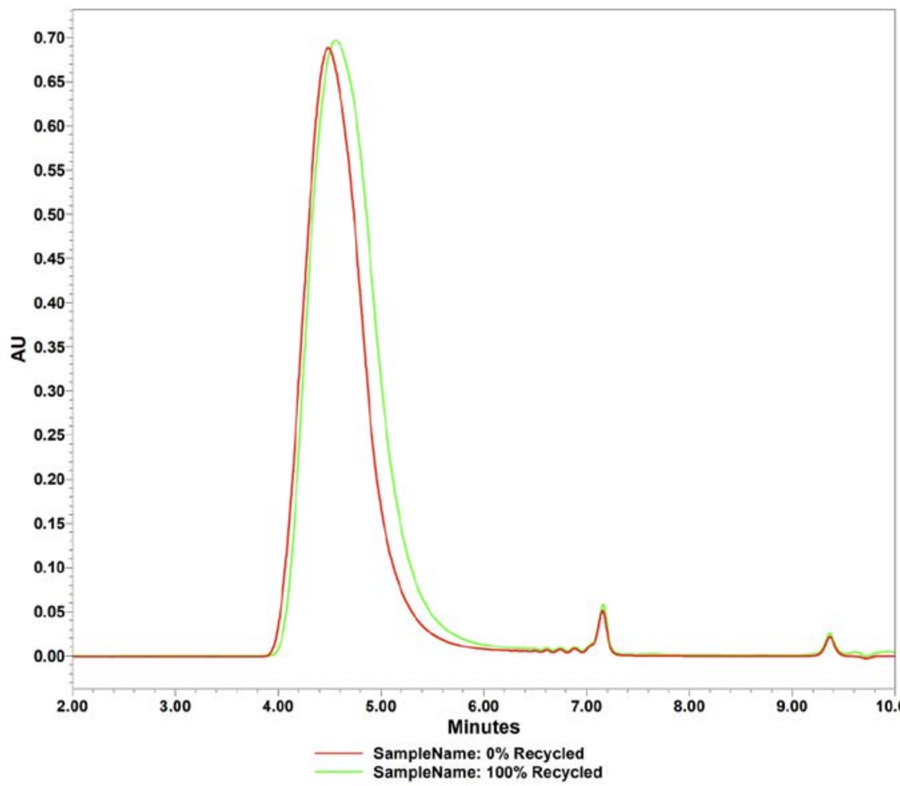

Figure 6. APC chromatographic results of 0% and 100% recycled polyamide gear samples. As more recycled material is added, the peaks have a higher retention time and slightly lower and broader shape. This change in shape change indicates a lower molecular weight and a broader molecular weight distribution.

Table 4. APC sample results from the 0% and 100% recycled polyamide gear samples

Sample Name	Retention Time (min)	Mn (g/mol)	Mw (g/mol)	MP (gmol)	Mz (g/mol)	Polydispersity
0% Recycled	4.487	36,342	148,999	125,645	332,214	4.10
100% Recycled	4.564	30,971	111,982	97,290	239,448	3.62

The APC system, with an ACQUITY APC XT™ column bank, enables the HFIP size separation of polyamides in 15-minutes from sample to sample *(Figure 6)*.

In addition to high pressure capability, the APC XT columns are resistant to solvent swelling unlike traditional SDVB columns. The SDVB column particles will swell and shrink when changing solvents, which changes the chromatography and can affect the column bed and, ultimately the analytical results. The advantages of using the APC option over a HT GPC is a three-fold time savings and six times less solvent consumption *(Table 5)*.

Table 5. Comparison of HT GPC, traditional GPC, and APC in regard to total analysis time and solvent use

GPC System	Mobile Phase	Run Temp (°C)	Flow rate (mL/min)	Analysis Time (min)	Solvent mL/Analysis	Column Particle
HT	ODCB	145	1	45	45	SDVB
HPLC	HFIP	50	0.5	45	22.5	SDVB
APC	HFIP	50	0.5	15	7.5	BEH

UNKNOWN IDENTIFICATION WITH PYROLYSIS-ATMOSPHERIC PRESSURE GAS CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY (py-APGC-HRMS)

Pyrolysis coupled to gas chromatography-mass spectrometry (py-GC-MS) is a common technique for the analysis of materials not amenable to solubilization. [6] The high energy of electron ionization (EI) used by vacuum GC-MS instruments, however, leads to significant molecular ion fragmentation which makes identification of unknown compounds difficult. Pyrolysis-GC with soft ionization high resolution mass spectrometry (HRMS) can help address some of these limitations. APGC is an ionization technique which uses a corona discharge enabling softer ionization. This results in molecular ion detection with little fragmentation which can help with the elemental composition confirmation. Moreover, APGC coupled to time-of-flight mass spectrometer (ToF MS) can acquire data in MS^E mode, whereby both low and high collision energy spectra are simultaneously acquired. This way, the accurate mass of both precursor and fragment ions are available to provide information for structural elucidation and ultimately aid compound identification. [7]

To investigate if the virgin and regrind materials differ in terms of their chemical fingerprint, samples were acquired on a pyrolyzer (EGA/PY-3030D, FrontierLab) coupled to APGC and a Xevo™ G2 XS QTof (equivalent or better performance is expected if a Xevo G3 QTof instrument is used) high resolution mass spectrometer. The resulting data was evaluated using multivariate statistical analysis, EZInfo™, out of the UNIFI™ application within the waters_connect™ platform. Three groups of samples were analyzed, each in triplicate: blanks (empty pyrolysis sample cups with quartz wool), virgin gears (0% RG), and 100% recycled gears (100% RG). To enable the identification of clusters, groups, and outliers a principal component analysis (PCA) model was initially constructed from the chromatographic data *(Figure 7A).*

An S-Plot of this data, *Figure 7B*, was then generated where the compounds at the extremes of an S-Plot represent markers that contribute highly to the discriminant separation model with high reliability. Those markers considered unique to each sample were subjected to further processing using the elucidation toolkit within the UNIFI™ application.

"One reason why certain OEMs don't allow the use of recycled polymers in safety critical components is the residual based uncertainty. By using py-GC-High Res MS recycling connected markers can be identified and thus shed light on the dark."

Pascal Tuszewski, Project Manager
Transmission Development at thyssenkrupp Presta AG

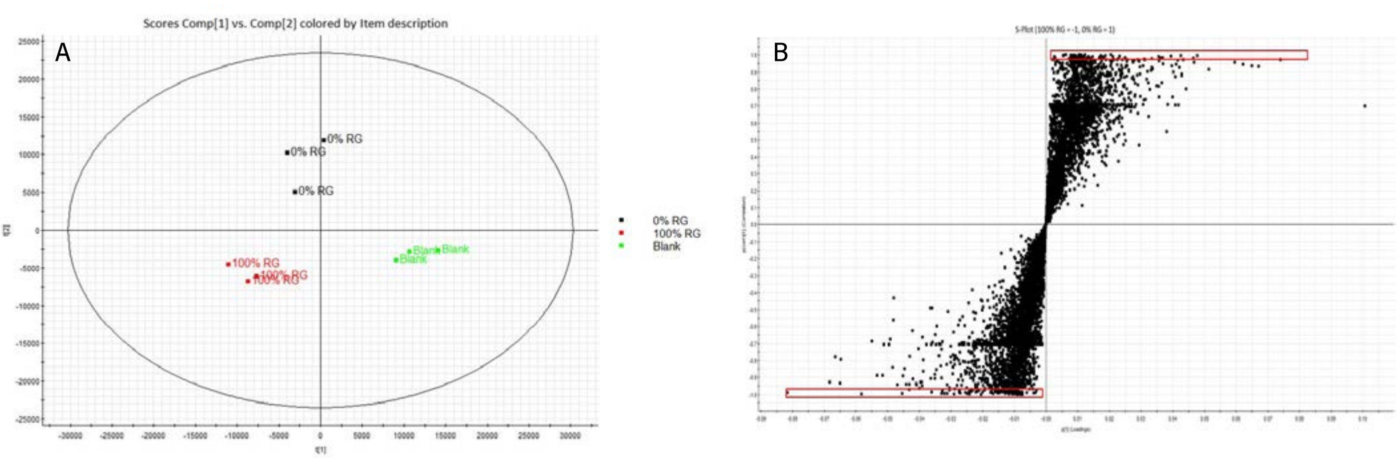

Figure 7. PCA scores scatter plot originating from py-APGC-QToF data (A). The first two principal components clearly separate blanks, virgin gears and 100% recycled gears. S-plot (B) of the 0% vs 100% recycled gear markers indicating statistically significant (P<0.05) markers for virgin (upper right) and 100% recycled (lower left) gears.

The toolkit utilizes all the data collected by the instrument. It starts with an elemental composition calculator that uses an i-FIT algorithm to score likely chemical formulas by the likelihood that the theoretical isotope pattern of the formula matches a cluster of peaks in the spectrum, along with the high-resolution accurate mass measurement. The software then undertakes database searches, for example in ChemSpider, with the predicted elemental composition.

An in-silico fragmentation is undertaken of the found structure to look for matches of the theoretical fragments with the observed high energy ions that were obtained using MS^E.

The pyrolyzates markers can be identified with different levels of confidence and an example of identification for one of the unique markers present in the 100% recycled gear is highlighted *(Figure 8).*

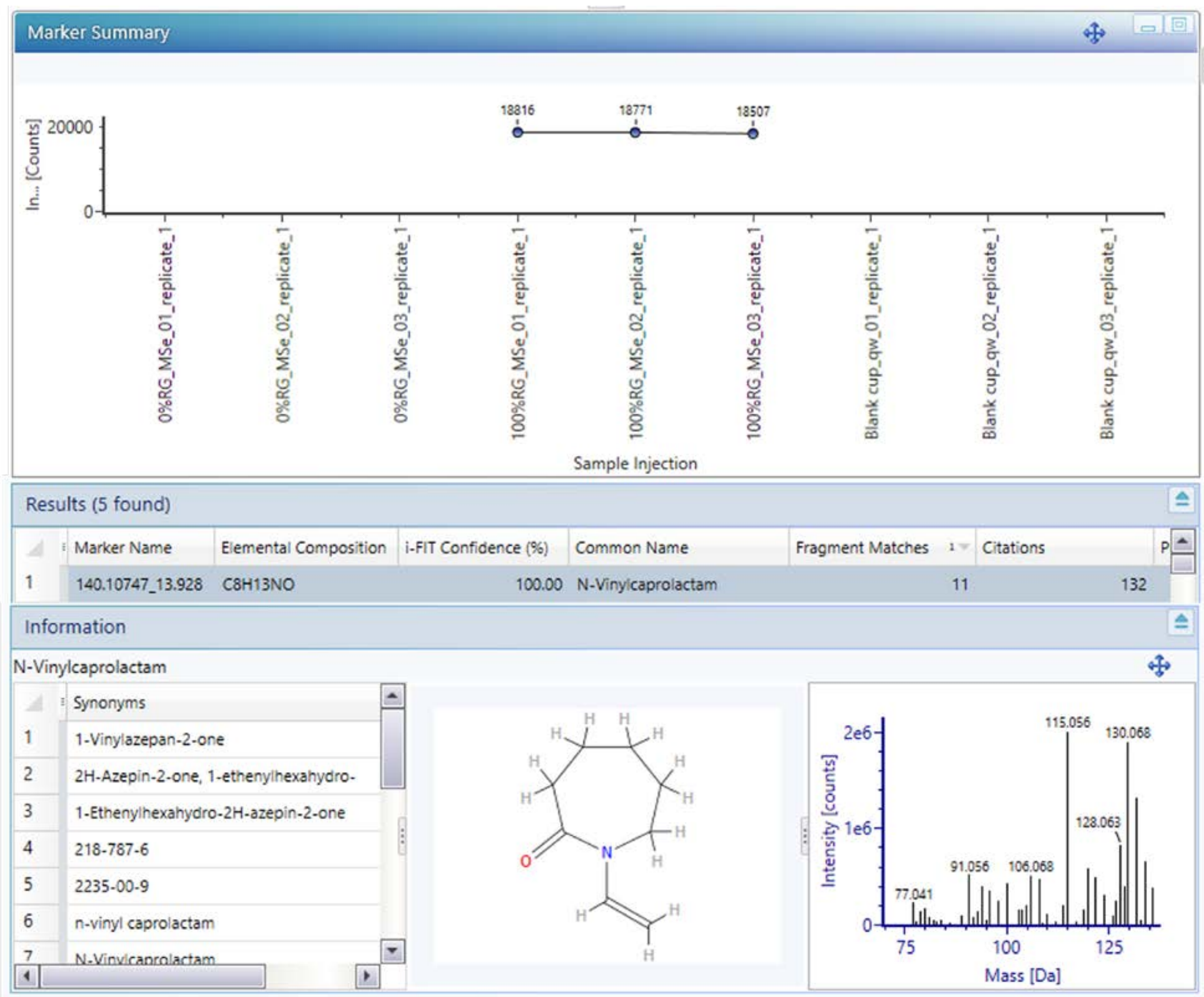

Figure 8. Putative identification of a marker (m/z_RT pair) unique in 100% RG sample as N-vinylcaprolactam at RT = 13.93 minutes with m/z 140.1075 ($[C_8H13NO]$+H mass error -0.2 ppm). Top pane represents marker abundance (response) in each of the 100% RG samples analyzed. Listed below are the results found for this marker; the predicted elemental composition, i-FIT confidence, common name for the compound, number of fragment matches, and the number of citations found. The bottom pane shows some of the synonyms for this compound, the structure, and high energy spectra.

SUMMARY

Developing sustainable products is an area of growing interest for many industries actively seeking new ways to incorporate recycled materials into their products.

In order to have a clear representation of the advantages of using recycled plastic, it is important to understand the raw material and product chemical composition as well as the final material performance.

When manufacturing polyamide gears, waste generated during molding process can be reground and mixed with the virgin materials without generating significant mechanical properties (data not shown here) or material appearance modification. This is due to the good melt stability of polyamide that allows it to maintain its molecular mass and mechanical properties even after having been subjected to several reprocessing cycles.

Additional insights into the material properties and chemical composition were obtained as follows:

- TGA data indicates the 100% gear and pellets are less thermally stable than the 0% gear and pellets. DSC data show that enthalpic relaxation occurs in the samples.
- The APC results confirm that a lowering of molecular weight of the highest peak (MP) occurs when the gear is sourced from 100% regrind material versus virgin materials (0% recycled gear MP = 126 KDa and 100% recycled gear MP = 97 KDa). The lower MP values agree with TGA results indicating a maximum mass loss rate at a temperature approximately 20 °C lower than the other samples, which could contribute to a product failure due to loss of heat resistance.
- Py-APGC-HRMS in combination with multivariate statistical analysis allows for confident analysis of unique markers in the regrind plastic gear samples. Furthermore, S-plot analysis isolated significant markers responsible for sample differences and the toolkit within the UNIFI application allowed for tentative compound identification using the power of soft ionization and high-resolution accurate mass measurements.

Taken together, analytical technologies such as TGA, DSC, SEC/GPC and py-APGC-MS are complementary analytical tools, useful to understand the structure and properties of a material. This approach helps answering questions such as how much recycled plastics to use, how to optimize the materials and, ultimately to ensure the manufacturing of successful and safe products.

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