Identification Method of Solid Waste Characteristic for Imported Recycled Engineering Plastics

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Abstract. The nitrogen content in imported recycled plastic particles was determined by elemental analyzer method and Kjeldahl method, respectively, and the acrylonitrile content was obtained by conversion to obtain the information on the consistency of polymer composition in recycled plastic particles. Two specific cases judged by this method were given. This method was available to provide a creative idea and method for the identification of solid waste characteristic of recycled engineering plastic particles containing acrylonitrile monomeric units such as acrylonitrile-styrene copolymer (SAN) recycled particles, acrylonitrile-butadiene-styrene copolymer (ABS) recycled particles, PC/ABS alloy recycled particles, PBT/ABS alloy recycled particles, PMMA/AS alloy recycled particles.

1. Introduction

Imported recycled plastics are the products based on the ban of the entry for "foreign garbage" waste plastics. Traders acquire the waste plastics garbage generated by developed countries and are transported to China for sale after cleaning, sorting, melting and regranulation in developing countries such as Southeast Asia. The quality of these imported recycled plastics is often uneven, and the source is very complex. Many of them are only simple primary processing products of waste plastics without any quality control conditions, and some may come from domestic plastic rubbish that is not sorted or washed clean, waste plastics that degrade seriously after multiple uses, and even medical plastic rubbish carrying high-risk substances. The import of these low-end inferior recycled plastics into China will pose a serious threat to the ecological environment and people's health of the country. It must be strictly supervised as a solid waste prohibited from importation, and it is rejected from the country. How to identify the solid waste attributes of imported recycled plastics is the key to prohibit the entry of "foreign garbage".

The consistency of the polymer composition of recycled plastics is an important evidence to determine whether it belongs to the rough processed recycled plastics or offcut and scrap produced during the production and processing of recycled plastics, or even the recycled plastic particles that have been fully processed. For recycled engineering plastics with complex composition, conventional analytical methods are difficult to apply [1-5], Fourier transform infrared spectroscopy (FT-IR) requires qualitative and quantitative analysis of specific functional groups, and is easily affected by various
additives and matrix in recycled plastics; near-infrared spectroscopy (NIR) requires the establishment of a series of sample libraries, which is difficult to achieve for the identification of recycled plastics with complex sources; differential scanning calorimetry (DSC) is difficult to analyze the composition by glass transition for the majority of engineering plastics are non-crystalline polymers with glass transition only while without melting process.

Common engineering plastics include acrylonitrile-styrene copolymer (SAN) recycled particles, acrylonitrile-butadiene- styrene (ABS) recycled particles, PC/ABS alloy recycled particles, PBT/ABS alloy recycled particles, PMMA/AS alloy recycled particles. Through the analysis of polymer monomers, it was found that the above polymers contain acrylonitrile monomer units. The information of sample consistency could be obtained by detecting the acrylonitrile content in the above recycled engineering plastics, providing data support for the subsequent identification of solid waste attributes.

The content of acrylonitrile in the polymer was available to be converted by detecting the nitrogen content in the polymer, while Kjeldahl method and elemental analyzer method were included in the common methods for determining the nitrogen content. The standards for using elemental analysis included GB/T 30733-2014 (Determination of total carbon, hydrogen and nitrogen content in coal- Instrumental method)[6], GB/T 19143-2017 (Analytical method of element of carbon, hydrogen, oxygen and nitrogen in rock organics) [7], and NB/SH/T 0656-2017 (Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants) [8], which were applicable for coal, organic matter in rocks and petroleum products, respectively; The standards for Kjeldahl method included GB 5009.5-2016 (National Food Safety Standard Determination of Protein in Food) [9] and GB/T 6432-2018 (Determination of crude protein in feeds – Kjeldahl method) [10], with the scope of application of food both. None of the above relevant standards were applicable to recycled plastics, so it was necessary to study the method suitable for the determination of nitrogen content in recycled plastics.

2. Experimental part

2.1. Instruments and reagents

Instrument: Vario EL cube (Elementar, Germany) ; Nexus Fourier Transform Mid-Infrared Spectrometer (Thermo Fisher Scientific, USA) ; DSC 3+ Differential Scanning Calorimeter (Mettler Toledo, Switzerland) ; KJELPEC 2300 Automatic Kjeldahl nitrogen analyzer (FOSS, Switzerland); Multifuge X1R High-speed Centrifuge (Thermo, USA) ; XP205 analytical balance (Mettler Toledo, Switzerland).

Reagents: Chloroform, Copper sulfate, Potassium sulfate, sulfuric acid, 30% hydrogen peroxide (Spectral Purity, Shanghai Reagent I Plant).

Standard materials: Sulfanilamide (N: 16.25% ; C: 41.81%, 18.62% ; H: 4.65% ) (Elementar, Germany).

2.2. Elemental Analyzer Method

2.2.1. The FT-IR was performed with instrument analysis conditions of: ATR/transmission, wavenumber: 400-4000 cm⁻¹, scanning times: > 32, and -CN cyanyl characteristic peak at 2260-2215 cm⁻¹. It was confirmed that the sample was a polymer containing acrylonitrile, and the main component of the sample was confirmed followed by search of spectrum.

2.2.2. Differential scanning calorimetry analysis was carried out, and the instrument analysis conditions were as follows: programmed temperature: start at 20°C, increased the temperature at a rate of 20°C per minute to 320°C and kept for 5 minutes, then decreased it at a rate of 20°C per minute to 20°C and kept for 5 minutes, after that, increased the temperature at a rate of 20°C per minute to 320°C for 5 minutes. Nitrogen atmosphere, flow rate of 50 mL/min, weighed 2-5 mg of sample. The glass transition temperature of the sample was between 85-125°C as polymer or co-mixture containing acrylonitrile.
2.2.3. Elemental analyzer was used to test the nitrogen content in the sample. The analysis conditions were as follows: high-purity helium pressure: 0.15-0.25 MPa; high-purity oxygen pressure: 0.20-0.03 MPa; combustion furnace temperature: 1000-1300°C, reduction furnace temperature: 700-900°C, sample size: 5-15 mg, oxygen transit time: 20-60 seconds.

2.2.4. The calculation formula of acrylonitrile content in the sample was as follows:

\[
C_A = 53 \times \frac{m_N}{14}
\]  

where 
\( m_N \) = the percent of nitrogen in the sample, mass %,
\( C_A \) = the percent of the monomer unit of acrylonitrile in the sample, mass %.

2.3. Kjeldahl Method

2.3.1. 0.2-2 g of the sample was weighed to the nearest 0.1 mg and put into a digestion tube. Then 0.4 g of copper sulfate, 6 g of potassium sulfate, 10-20 mL of sulfuric acid and 1-5 mL of hydrogen peroxide were added for digestion.

2.3.2. Given that the temperature of the digestion furnace reached 400-500 °C, continue heating for 1-4 hours until the liquid in the digestion tube appeared green and transparent.

2.3.3. After taking out the digestive tube, 20-50 mL of water was added and placed in the automatic Kjeldahl apparatus for the process of automatic liquid addition, distillation, titration and recording of titration data.

2.3.4. The calculation formula of acrylonitrile content in the sample was as follows:

\[
C_A = \frac{53}{14} \times \frac{(V_1-V_2) \times c \times 140}{m \times V_3}
\]

where 
\( C_A \) = the percent of the monomer unit of acrylonitrile in the sample, mass %,
\( V_1 \) - The volume of standard volumetric solution of sulfuric acid consumed by test solution, mL;
\( V_2 \) - The volume of standard volumetric solution of sulfuric acid consumed by the reagent blank, mL;
\( c \) - The concentration of standard volumetric solution of sulfuric acid, mol/L;
\( m \) - The sample mass, g;
\( V_3 \) - The volume of the digestive juice sucked, mL.

3. Actual Sample Analysis

3.1. Identification of Solid Waste Characteristic of PC/ABS Alloy

At the beginning of 2019, an importer imported a batch of goods with the application product name of PC/ABS alloy recycled particles from Malaysia and was sent to the laboratory for solid waste characteristic identification for the inclusion of particles of other colours in the sample. The sample was black plastic particle and mixed with white particle and green particle. The black particle was composed of single particle and heterogeneous particle bonded together. The photos are shown in Figure 1:
The enterprise claimed that it belonged to plastic recycled material. After sorting, cleaning and disinfection, the recycled particles were remelted and melted to be applied in mobile phone shell, computer and commercial machine shell, electrical equipment, lawn gardening machine and automobile parts dashboard.

Infrared spectroscopy and differential scanning calorimetry were used to test the polymer composition in the samples, and it was found that the main components of the particles were acrylonitrile-butadiene-styrene copolymer and co-mixture of polycarbonate (PC/ABS alloy). The specific information of the polymer composition could not be obtained by the conventional method. Considering that the samples contained acrylonitrile, the composition of the polymer could be confirmed by converting the acrylonitrile content by the determination of nitrogen content, thus the above two methods were used to detect the particles of different colours. The results are shown in Table 1:

| Item                  | Black particles | Green particles | White particles |
|-----------------------|-----------------|-----------------|-----------------|
| percent of nitrogen,  | 2.8             | 1.9             | 7.2             |
| mass%                 | 2.67            | 1.81            | 7.06            |
| percent of acrylonitrile, mass% | 10.6 | 7.2 | 27.3 |
| mass%                 | 10.1            | 6.9             | 26.7            |

It was found that the nitrogen content of the three particles was different, with varied acrylonitrile content, therefore, the polymer composition of the particles with different colours was judged to be...
inconsistent. It might be a mixture of recycled particles of different specifications. Combined with the results of ash, the subject was comprehensively considered as a waste plastic particle mixed with different colours and different compositions after processing treatment and belonged to solid waste.

3.2. Identification of Solid Waste Attributes of Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene Polymer (MABS)

At the end of 2019, an importer imported a batch of goods with the application product name of methyl methacrylate-acrylonitrile-butadiene-styrene polymer (sub-brand) recycled particles from Taiwan and sent them to the laboratory for solid waste attribute identification considering a small amount of colour difference in the particles.

The sample was colourless and translucent plastic particles, mixed with purple and translucent particles with uniform particle size. As shown in Photo 2:

![Original photo of sample](image)

(a) colourless translucent particles after sorting

(b) purple translucent particles after sorting

Fig. 2 Recycled plastic particles of Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene Polymer (MABS)

The enterprise claimed that the colour difference and melting finger instability occurred for the failure of technology during production or the switch of production line, which was designated as a sideline material when it left the factory and was used to make household items. Therefore, it was possible for the sample to be mixed for two different production purposes of the plastic particle.

Infrared spectroscopy and differential scanning calorimetry were used to test the polymer composition in the samples, and it was found that the main components of the two particles were methyl methacrylate-acrylonitrile-butadiene-styrene copolymer (MABS). Considering that the samples contained acrylonitrile, the acrylonitrile content could be converted by measuring the nitrogen content, so the above two methods were used to detect the particles of two different colors. The results are shown in Table 2:

| Item                          | colourless translucent particles | purple translucent particles |
|-------------------------------|---------------------------------|-----------------------------|
| percent of nitrogen, mass%    | 2.9                             | 1.6                         |
| percent of acrylonitrile, mass% | 11.0                            | 6.1                         |

It was found that the nitrogen content of the two kinds of particles was different, and the acrylonitrile content was different. Therefore, it was judged that the polymer composition of the particles with different colors was inconsistent. It should be the mixing of recycled particles with different specifications. Combined with the results of melt mass flow rate (MRF), it was comprehensively judged that the samples were the mixing of plastic particles with different production purposes, colours and components during the plastic production and processing, which belonged to solid waste.
4. Conclusion
It was difficult to obtain the polymer composition information of recycled engineering plastics by conventional infrared spectroscopy, differential scanning calorimetry, thermogravimetry and other methods, while the nitrogen content in recycled engineering plastics could be effectively detected by elemental analyzer method and Kjeldahl nitrogen method. Moreover, the composition information of polymers in the samples could be obtained by nitrogen content conversion, from which the consistency of polymer composition in the samples could be inferred. Besides, the results determined by different methods also presented a good correlation, providing a idea and method for the identification of solid waste attributes of recycled engineering plastic particles containing acrylonitrile monomeric units such as acrylonitrile-styrene copolymer (SAN) recycled particles, acrylonitrile-butadiene-styrene (ABS) recycled particles, PC/ABS alloy recycled particles, PBT/ABS alloy recycled particles, PMMA/AS alloy recycled particles at this stage. Apart from that, it provided technical support for the identification of solid waste attributes of recycled plastics.

Acknowledgements
This work was financially supported by the science research project of General Administration of Customs, P. R. CHINA (Fund No.: 2019HK016 and 2020HK245), the Ningbo public science research project (Fund No.: 2019C50031) and the Zhejiang basis public science research project (Fund No.: LGC20B040001).

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