Solid waste characteristic identification method of imported epoxy resin

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Abstract. Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimeter (DSC) and various analytical methods were used to analyze the main components, glass transition temperature (Tg), volatile matter content and ash content of a batch of imported recycled epoxy resin. According to the appearance characteristics and the production process of the sample, the source of the sample was analyzed, Solid waste properties were determined according to the relevant provisions of GB 34330-2017 "Identification standards for solid wastes General rules". The results show that the samples belong to epoxy resin scrap and trim mix manufactured by different production processes for different production purposes, which fall in the category of solid wastes banned by China for import. This identification method provides a reference for the identification and supervision of solid waste derived from imported recycled plastics.

1. Introduction
With the rapid development of China’s economy, various resource shortages have occurred from time to time. Therefore, China has become a major importer of reusable resources. For these reusable resources, the state has set a list of solid wastes that can be used as raw materials for non-restricted imports. The cargo stipulated by the state to be included in the list of non-restricted imports of solid wastes that can be used as raw materials may not be regulated according to solid waste. The cargo listed in the list of solid wastes that can be used as raw materials are imported and approved for import. The cargo in the waste catalog are prohibited from being imported. Therefore, for cargo suspected of solid waste in the process of customs supervision, it is necessary to carry out the identification of solid waste properties to determine whether they can be imported. The national standard GB 34330-2017 “Identification standards for solid wastes General rules” is one of the main basis for the identification of solid waste properties[1,2].

Recycled plastics are plastic products made by recycling, sorting, cleaning, and melting granulation, which can be used to produce low-end plastic products. If the plastic regeneration process is not strictly controlled, the recycled plastics thus produced may have high environmental pollution risks and safety impacts[3,4]. Therefore, only solid wastes, which meet the imported environmental protection control standards for raw materials, and matter, which conforms to the national or local standards or the general industry product and quality and is intended for its original use, can be imported, and the rest shall be supervised as solid wastes. Plastic solid waste imported by some traders in the name of recycled plastics will cause greater harm to China’s ecological environment. With
China’s continued efforts to combat the import of “foreign waste”, the identification of plastic solid waste and recycled plastics will be more and more important. There is little literature on the identification of imported plastic solid waste. A batch of typical epoxy solid wastes seized by the customs as is used an example in this case study, and infrared spectroscopy (FT-IR)[1], differential scanning calorimeter (DSC), volatile matter, ash content and source analysis method, etc., are used to determine the properties of solid waste. The results can provide powerful technical support for solid waste supervision by the customs, and provide reference for the identification of imported plastic solid wastes properties.

2. Experimental

2.1 Instrument

Nexus Fourier Transform Mid-Infrared Spectrometer (Thermo Fisher Scientific, USA); DSC 3+ Differential Scanning Calorimeter (METTLER TOLEDO, Switzerland); LC-220 Blasting Oven (Shanghai Espec, China); ML204 analytical balance (METTLER TOLEDO, Switzerland); CWF11/23 muffle furnace (Carbolite, UK).

2.2 Sample sorting

The sample is packed in a plastic bag with a customs seal. After unsealing, the sample is poured into a large ceramic disk. The sample is in various forms (as shown in Fig.1), and representative samples are numbered according to the appearance and color of the sample (as shown in Fig.2).

2.3 Infrared spectroscopy

Some representative samples are viscous and are not suitable for post-crushing for pressing potassium bromide troche. Melt pressing films may cause oxidation and solidification. For this reason, it is not suitable for use. Therefore, Attenuated Total Reflection (ATR) analysis is directly used to analyze the main components and conditions: ATR analysis, with a wave number of 50-4000 cm⁻¹, and there reflective medium being diamond.

2.4 differential scanning calorimeter

The representative samples are cut into small pieces, which are then pressed into a thin film at a thickness of about 200 µm ± 20 µm, which is in turn cut into a small piece. The representative sample with a mass of 4 mg ± 2 mg is placed in a 40 µL aluminum crucible, sealed and punched with a hole. Thermal analysis is conducted using a differential scanning calorimeter, DSC parameters: temperature program is constant at 50 °C for 1 min, and then risen to 150 °C at a heating rate of 20 °C per minute, and then kept constant for 2 min. Then, the temperature is lowered to 50 °C at a rate of 20 °C per minute and kept constant for 2 min, and then increased to 150 °C at a rate of 20 °C per minute, and kept constant for 5 min. The carrier gas is nitrogen, and the gas flow rate is 50 mL/min.

2.5 volatile matter content

According to the requirements of 5.8 of GB/T 13657-2011 “Bisphenol-A epoxy resin”, the volatile matter content is measured. First, various representative samples are crushed, and passed through a 2 mm sieve. Next, 1 g ± 0.1 g of samples weighed, accurate to 1 mg, and placed in a glass-surface vessel (with an inner diameter of 75 mm ± 5 mm, and an edge height > 5 mm) after constant weight. Then, the glass-surface vessels placed in a forced air blasting oven at 150 °C for 60 min. After the heating is over. The glass-surface vessels transferred to a dryer and allowed to cool to room temperature and weighed again to calculate the volatile matter content of the representative samples.

2.6 Ash test

The ash content of the sample is tested according to GB/T 7531-2008. 25 g±1 g of each representative samples weighed, and placed in a crucible after constant weight. Next, the crucible containing the
sample is slowly heated on the electric furnace until the sample has been all carbonized. Then, the crucible is transferred to a muffle furnace at 850 °C, and fired at a high temperature for 60 min. After the burning time is completed, the crucible is taken out to a dryer, cooled to room temperature, and weighed again to calculate the ash content of the sample.

3. Results and discussion
Each representative sample exhibits a variety of morphological appearances and colors. The representative sample numbers and their descriptions are given in Tab. 1 below:

| Number | Description |
|--------|-------------|
| 1      | colorless and transparent small granular plastic particles |
| 2      | colorless and transparent small piece |
| 3      | colorless and transparent curved strip samples |
| 4      | yellowish transparent block sample |
| 5      | yellow transparent block sample |
| 6      | milky white plastic block sample |
| 7      | milky white gel block sample |
| 8      | light yellow crystal condensate sample |
| 9      | yellowish-like stone-like cement samples |
| 10     | yellow-like stone block samples |

Fig.1 Photo of the original sample

Fig.2 The representative sample numbered after sorting
3.1 Infrared spectroscopy analysis of samples

Due to the large number of samples, samples are divided into three groups. The infrared spectrum of each group is shown in Fig.3, Fig.4 and Fig.5, respectively:

![Fig3. Infrared spectra of representative samples 1, 2, 3, 7, and 8.](image)

The infrared spectra of representative samples No 1, 2, 3, 7, and 8 in the first group are similar, and their spectrum are analyzed. The C-H group near the 750 cm⁻¹ is bending vibration absorption peak; close to 950 cm⁻¹ C-O of oxirane group stretching absorption peaks, C-O-C ester group near 1050 cm⁻¹ stretching vibration absorption peak, C-C stretching vibration absorption peak around 1250 cm⁻¹, and phenyl group absorption peak around 1500 cm⁻¹, which may result in a serious baseline offset of the sample due to the presence of impurities in the sample. The sample may be a bisphenol-A epoxy resin according to comparison with a standard library[5].

![Fig4. Infrared spectra of representative samples No. 6, 9, and 10.](image)

The second group includes representative samples No. 6, 9, and 10. The infrared spectrum are relatively close, and there may be fewer additives. Therefore, the baseline is flat. Similar to Fig.1, in addition to a 750 cm⁻¹ C-H group, a 950 cm⁻¹ C-O group, a 1050 cm⁻¹ C-O-C epoxy group, a 1250 cm⁻¹ C-C group, and a 1500 cm⁻¹ phenyl group absorption peak, it can be clearly observed that the C-O-C epoxy group stretching vibration near 850 cm⁻¹ and the absorption peak of the benzene ring at about 2900 cm⁻¹. Therefore, the sample may be a bisphenol-A epoxy resin.
The third group is the infrared spectra of representative samples No. 4 and No. 5. In addition to the characteristic absorption peaks of the epoxy resins analyzed in Fig. 1 and 2, it can be seen in Fig. 5 that the samples No. 4 and 5 show characteristic absorption peak of the -CN cyano group around 2050 cm\(^{-1}\); the absorption peak of the benzene ring near 2900 cm\(^{-1}\), and the absorption peak of the -NH amino stretching vibration of 3500 cm\(^{-1}\). The sample may be an epoxy resin to which an amine curing agent is added.

3.2 Thermodynamic analysis of the representative samples

The temperature-increasing section is analyzed after relieving the heat history of each representative sample, and the thermal analysis spectrum of each representative sample is shown in Fig. 6 and Fig. 7:

![Thermal analysis spectrum of No. 1-5 representative samples](image-url)
As can be seen from Fig. 6 and 7, as samples No. 9 and 10 have no glass transition temperature, they may be oligomers of bisphenol A epoxy resin, and each of the other samples has a glass transition temperature and is different. The thermal analysis curve of samples No. 2, No. 6, and No. 7 has a relaxation phenomenon, indicating that there may be crystals in the sample, the molecular chain starts to move, and an additional exothermic peak is generated by crystal destruction[6,7].

3.3 Analysis of physical and chemical properties

The results of infrared characterization, thermal analysis of glass transition temperature, volatiles, ash, etc. are summarized in Table 2:

| No. | Infrared Qualitative            | Glass transition temperature, °C | Volatiles matter content % (mass fraction) | Ash % (mass fraction) |
|-----|---------------------------------|----------------------------------|-------------------------------------------|-----------------------|
| 1   | Bisphenol-A epoxy resin         | 93                               | 1.4                                       | 0.02                  |
| 2   | Bisphenol-A epoxy resin         | 61                               | 1.0                                       | 0.02                  |
| 3   | Bisphenol-A epoxy resin         | 93                               | 1.2                                       | 0.02                  |
| 4   | Bisphenol-A epoxy resin         | 62                               | 1.6                                       | 0.05                  |
| 5   | Bisphenol-A epoxy resin         | 87                               | 0.6                                       | 0.05                  |
| 6   | Bisphenol-A epoxy resin         | 61                               | 0.9                                       | 0.02                  |
| 7   | Bisphenol-A epoxy resin         | 77                               | 0.7                                       | 0.08                  |
| 8   | Bisphenol-A epoxy resin         | 70                               | 0.8                                       | 0.07                  |
| 9   | oligomers of epoxy resin        | /                                | 0.5                                       | 0.02                  |
| 10  | oligomers of epoxy resin        | /                                | 0.7                                       | 0.02                  |

As can be seen from the above table, the volatile matter content of each sample is different, and the other samples do not meet the requirements except Sample No.9, according to minimum requirementson volatile matter content(<0.6% (mass fraction) in GB/T 13657-2011 “Bisphenol-A epoxy resin” standard. Also, the ash content of each sample is not high.

4. Summary

Through the above analysis, combined with the sample appearance, texture and color, the possible sources of the sample can be analyzed. The representative sample No. 1 is the finished epoxy resin.
plastic particles; the representative sample No. 2 is the scrap of the epoxy resin sheet material; and the representative sample No. 3 is the extruded elongated scrap generated during the extrusion granulation process in the production process of the epoxy resin pellet; the representative samples No. 4 and 5 are epoxy resin blocks added with an amine curing agent; the representative samples No. 6, 7 and 8 are the epoxy resin scraps of various specifications, and the representative samples No. 9 and 10 are oligomeric epoxy resin. On the whole, the samples are the scrap and trim produced in the production process of various epoxy resins. And their volatiles matter content do not meet the minimum requirements of GB/T 13657-2011 “Bisphenol-A epoxy resin” standard. According to 4.2 of GB 34330-2017, the samples are determined to be scrap, trims, residual materials, etc. produced during the processing and manufacturing process of the resin product. In short, the samples are determined to be solid wastes and should not be imported.

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