Pyrolysis-gas chromatography/mass spectrometry to identification of the solid waste characteristic of imported polyamide recycled plastics

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Abstract. An analytical method for the determination of content of PA66 in PA6/PA66 blends by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) with silica (SiO₂) as dispersant was established. After the sample was frozen and crushed into powder, silica was used as a solid dispersant mix with the sample, and the mixtures was injected. At 600°C cracking temperature, the corresponding cracking chromatogram was obtained, and the characteristic of PA66 on the cracking chromatogram of PA6/PA66 blend, the cyclopentanone, was selected as the quantitative peak to calculate the mass of PA66 in the PA6/PA66 blend. The content of PA66 in the dispersion was in the range of 0.50 g/kg ~ 100 g/kg, and the results had a good linear relationship. The detection limit of the PA66 was 0.50 g/kg (the corresponding PA66:PA6 ratio was 0.5:99.5). The PA6/PA66 samples with known mixing ratio were measured, and the recovery of the results was 95.7%~102.1%, and the relative standard deviation(RSD) was 1.6%~5.9% (n=3). It can accurately determine the content of PA66 in PA6/PA66 blends, and provide technical support for the attribute identification of related imported recycled plastic solid wastes.

Introduction. Py-GC/MS; Recycled polyamide; Solid dispersant; Solid waste Characteristic identification

1. Introduction

With the implementation of "soid waste ban" from China, waste plastics exporting companies such as Europe and the United States have lost the world's largest solid waste market. Many companies have invested their production capacity in Thailand, Malaysia, Vietnam, Poland and other countries, where waste plastics are processed into recycled particles and then exported to the Chinese. Although importing waste materials from abroad can make up for the shortage of resources in China, driven by economic benefits, some foreign suppliers have mixed solid waste plastics with recycled plastic particles for customs declaration. How to make reasonable use of imported waste materials and recycled raw materials, and to effectively prevent the entry of "foreign garbage" into the country and
harm our country’s ecological environment and people's health, the identification of solid waste has become the key technology.

Polyamide is usually called nylon, which is mainly used in the production of films, fibers, engineering plastics, etc., and is the largest consumption of the five engineering plastics in the world so far. There are two main sources of waste of polyamide, one part is engineering plastics, discarded old carpets, tire cords, etc. Because this part contains more impurities, it is usually disposed by landfill or incineration, which is easy to cause environmental pollution and waste of resources. The other part is waste scraps, leftovers, etc., which is produced during production. These products have less impurities, so they can be melted and can be melted and pelletized for reprocessing[1].

There are many kinds of polyamides, among which Polycaprolactam (PA6) and Polyhexamethylene adipamide (PA66) are the main ones. PA6 and PA66 have similar chemical structures and good compatibility. Copolymerization or blending can reduce the hydrogen bond formation rate and crystallinity of the material, greatly enhance the thermal, physical and mechanical properties of the material, obtain PA with excellent comprehensive properties, and expand its application range. In general, infrared spectroscopy(IR), differential scanning calorimetry(DSC), thermogravimetric analysis(TGA), etc. can be used to characterize the polymer composition in the sample to complete the identification [2-5]. However, for plastic particles that are qualitatively pure PA6/PA66 blends and the content of additives contained is negligible, the ratio of PA66 and PA6 directly affects the classification. At present, there is no relevant standard for quantitative analysis of PA6/PA66 blend ratio.

Py-GC/MS is an important method to characterize the composition and structure of polymer materials. This technique does not require complex sample preparation, and can infer the structure and composition of the sample based on the qualitative and quantitative data of the cleaved compounds[6-8]. At present, some scholars have used Py-GC or Py-GC/MS to quantify PA6/PA66, PC/ABS, ABS/PA6 and other blends, but mainly use the peak area ratio relationship of characteristic pyrolysis products. For different ratio ranges of blends, different quantitative working curves are required [9-11]. Therefore, we developed and validated a new Py-GC/MS method for the quantification of PA6/PA66 blends by using silica as a solid dispersant for the preparation of readily measurable dispersion standards. This method is suitable for quantitative analysis of PA6/PA66 blends in a full range of ratios, and provides technical support for the identification of related imported plastic solid waste attributes.

2. Experimental

2.1 Instrument
7890B/5975C gas chromatography-mass spectrometer(Agilent, USA); PY-2020 iD pyrolyzer (Frontier, Japan); ZM200 High-speed universal crusher (Restch, Germany); SHL-52 twin screw extruder (Nanjing Highly, China); 3745 -ZHE mixer (ADM, USA).

2.2 Samples and reagents
Silica powder (analytical purity), after passing through a 120-mesh screen, ready for use. Polyamide 66 (PA66) plastic particles and polyamide 6 (PA6) plastic particles were frozen and crushed separately, and powder was obtained through a 120-mesh sieve to be used.

2.3 Preparation of dispersion standards
The PA6/PA66 blend was prepared by melt blending. First, PA66 powder and PA6 powder were mixed uniformly in a mixer according to different ratios. The mixing ratios of PA6/PA66 were: 0/100, 10/90, 20/80, 40/60, 60/40, 80/20, 100/0. Then fed to the twin screw extruder for blending, extruding and pelletizing. After freezing and crushing, it passed through a 120 mesh screen. Took 0.10 g of PA6/PA66 powder after sieving, added silica powder to 1.00 g, and mixed evenly. A series of PA6/PA66 dispersions with known blending ratios were obtained to establish the working curve. In
this series of standards, the mass of PA66 per 1 g of dispersion was 0.00 g, 0.01 g, 0.02 g, 0.04 g, 0.06 g, 0.08 g, and 0.10 g.

2.4 Sample preparation
The PA blend sample was freeze-crushed and passed through a 120 mesh screen to obtain a powder. Weigh 0.10 g of powdered sample, add silica powder to 1.00 g and mix evenly, to be tested.

2.5 Py-GC/MS operating conditions
The pyrolysis temperature was 600℃, the pyrolysis time was 1 min, and the interface temperature was 300℃. DB-5HT capillary column (30m×0.25mm with 0.10μm film thickness) was used. The GC-MS conditions were as follows: the initial temperature is 50℃, and the temperature is raised to 280℃ at a rate of 5℃/min and held for 0 minutes. The inlet temperature was 300℃ and the split ratio was 20:1. The solvent delay time was 2min. The carrier gas was high purity helium with a flow rate of 1.0 mL/min. The temperature of the chromatography- mass spectrometry interface was 280℃. The ionization method was EI, and the ion source temperature and quadrupole temperature were 230℃ and 150℃, respectively. Used full scan mode (SCAN) for qualitative, mass spectrum scan range: 29m/z-600 m/z. The selected ion monitoring mode (SIM) was used for quantification, and the characteristic quantitative ion was 84 m/z.

2.6 Establishment of working curve
The series of PA6/PA66 blend standards were weighed out at 0.005g each time for Py-GC/MS detection. The mass concentration of PA66 in the dispersion was taken as the abscissa, and the characteristic ion m/z=84 peak area of the characteristic peak of cyclopentanone after PA66 cracking was taken as the ordinate to establish a working curve.

2.7 Quantitative analysis
Weighed 0.005g of the dispersed PA6/PA66 blend sample into an inertized sample cup, and Py-GC/MS detection in the same way as the series of PA6/PA66 blend dispersion standards. Substituting the measured mass concentration of PA66 into formula (1) could obtain the content of PA66.

\[
w(\%) = \frac{c \times 100 \times m_1}{m}
\]

(1)

In formula (1), \(c\) was the mass concentration of PA66 in the sample after adding silica dispersant (calculated by linear equation); \(m_1\) was the mass of the sample after adding the dispersant, and \(m\) was the sample weighed before adding the dispersant quality.

3 Results and discussion

3.1 Selection of solid dispersant
In this study, silica powder and titanium dioxide powder were selected for investigation. The two dispersants did not crack in the temperature range of 100℃-700℃. However, when mixing with polymer powder, titanium dioxide powder was prone to the phenomenon of cohesion, which could not evenly disperse the sample and had poor reproducibility. While the silica could disperse the polymer uniformly, and the obtained cracking chromatogram had good reproducibility. Therefore, silica was selected as the solid dispersant.

3.2 Selection of characteristic quantitative peaks
Qualitative analysis of the corresponding characteristic peaks using spectral library search combined with manual analysis. Figure 1 A showed the pyrolysis chromatogram of PA66. The characteristic
peak obtained after the pyrolysis of PA66 was mainly cyclopentanone. Figure 1 B showed the pyrolysis chromatogram of PA6. The characteristic peak obtained after the pyrolysis of PA6 was mainly caprolactam. Figure 1 C showed the pyrolysis chromatogram of PA6/PA66 blend after silica dispersant was added. It could be seen from the figure that the characteristic peak of PA66 was relatively obvious and the response value was higher, so its characteristic ion M/z=84 was selected as the quantitative ion.

![Pyrolysis chromatograms of PA66(A), PA6(B) and PA6/PA66/SiO2](image)

**Fig.1 Pyrolysis chromatograms of PA66(A), PA6(B) and PA6/PA66/SiO2**

### 3.3 Selection of pyrolysis temperature

The pyrolysis temperature affects the generation and distribution of polymer pyrolysis products, which is very important for obtaining suitable characteristic pyrolysis chromatograms. When high polymer is cracked at low temperature, the degradation rate is slow, there are many high boiling point substances, and the gas chromatographic characteristic peak is not obvious. If the temperature is too high, it may break into too small fragments, which is not characteristic. The powder obtained by freezing and crushing the PA6/PA66 blend and sieving, weighed the same mass, and conducted the cracking reaction at different cracking temperatures. The content of cyclopentanone, the main characteristic product of PA66, changed with the pyrolysis temperature. When the cracking temperature was 600°C,
the content of the PA66 cracked product cyclopentanone was the largest, and the signal was stable without interference, so 600°C was chosen as the cracking temperature (as shown in Fig. 2).

![Fig.2 Pyrolysis chromatograms of PA6/PA66 blend at different pyrolysis temperatures](image1)

![Fig.3 Pyrolysis chromatograms of PA66/SiO2 at different dilution ratios](image2)

### 3.4 Selection of sample to dispersant ratio
When the powder in the sample cup does not exceed 1/3 of the cup body during the lysis process, it can effectively prevent the sample from splashing out of the cup during the instant falling process, and it can also ensure that the sample will not be brought into the analysis pipeline and cause blockage under the action of the carrier gas flow. At this time, the mass of the powder in the cup is 0.005g, which is used as the fixed sample injection amount after adding the solid dispersant. The fixed PA66 powder mass was 0.1g and silica powder was added to 1g, 2g, 5g, 10g, 20g to disperse, and the dilution ratio of PA66 powder and dispersant was 1:10, 1:20, 1:50, 1:100, 1:200 for investigation (see Figure 3). When the dilution ratio was 1:10, the chromatographic peak of cyclopentanone could be guaranteed not to split, and the sensitivity of the characteristic peak could be improved, and the detection limit of the method could be reduced. Therefore, the ratio of PA66 powder to silica solid dispersant was 1:10.

### 3.5 Method detection limit and linear relationship
The mass concentration of PA66 in the dispersion was taken as the abscissa, and the characteristic ion m/z=84 peak area of the characteristic peak of cyclopentanone after PA66 cracking was taken as the ordinate to establish a working curve. The results showed that: the mass concentration of PA66 in the dispersion was within the range of 0.50g/kg~100g/kg (corresponding to PA66:PA6 =0.5:99.5~100:0). There was a good linear relationship, and the correlation coefficient R² was 0.998. The detection limit of PA66 calculated by 5 times the signal-to-noise ratio (S/N=5) was 0.50g/kg (corresponding to PA6: PA66=99.5:0.5).

### 3.6 Precision test
Four samples of PA6/PA66 blends with known content were measured, and the recovery rate was 95.7%~102.1%. The relative standard deviation (RSD) of the three measurements was 1.6%~5.9%. The accuracy and precision of the method were good.

| Specimen               | Actual content of PA66, % | Measured results, % | Average results, % | Recovery, % | RSD, % |
|------------------------|---------------------------|---------------------|--------------------|-------------|--------|
| PA6/PA66 blend 1       | 30.7                      | 29.4, 31.5, 33.1    | 31.3               | 102.1       | 5.9    |
| PA6/PA66 blend 2       | 50.9                      | 50.1, 47.7, 48.3    | 48.7               | 95.7        | 2.6    |

Table 1. Accuracy and precision test of method (n=3)
3.7 Actual sample detection
In the middle of 2019, an importing company imported a shipment of recycled particles called light-grey recycled polyamide-66 practices from Vietnam, which was sent to the laboratory for identification of solid waste characteristic because of the inconsistent colour of the goods.

A sample of brownish yellow plastic particles, mixed with light-grey particles, uniform particle size, the main components of the two particles are polyamide, as shown in figure 4:

![Original photo of sample](image1)
(a) Brownish yellow particles after sorting
(b) Light-grey particles after sorting

Fig . 4 Recycled plastic particles of recycled polyamide

Particles of two different colours were tested separately according to the above method, and the results are shown in Table 2:

| Item                              | Brownish yellow particles | Light-grey particles |
|-----------------------------------|---------------------------|----------------------|
| Polymer composition, mass%        | Polyamide-6               | 94.8                 | 14.8                 |
| Ash, mass%                        | Polyamide-66              | 5.2                  | 85.2                 |

It is found that the composition of the two kinds of samples is completely different, which should be the mixture of different specifications of recycled particles. It is comprehensively determined that the sample is a mixture of plastic particles with different colors, components and melt mass-flow rate after processing, which belongs to solid waste.

4. Conclusion
This study provides a sample prepared by using inert solid powder as a dispersant for PA66/PA6 samples. The pyrolysis/gas chromatography-mass spectrometry method is used to quantitatively analyze the dispersed PA66/PA6 blend samples, and the PA66 characteristic cracking products The relationship between the peak area of cyclopentanone and the content of PA66 was established to establish a working curve, and the mass fraction of PA66 in the PA66/PA6 mixture was calculated, and then the mass fraction of PA6 was further calculated. The detection method is fast and accurate, and can realize the quantitative analysis of the full range ratio of PA66/PA6 blends. It provides a new method for the composition identification of imported recycled polyamide.

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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