Application of Instrumental in the Identification of Solid Waste Characteristic of Imported recycled ABS Plastic

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Abstract. The content of carbon, hydrogen and nitrogen in imported recycled ABS plastics was determined by Instrumental, and the content of three monomer units (acrylonitrile, butadiene and styrene) in ABS was calculated. The influence of sample quantity and combustion time was discussed. The precision of carbon, hydrogen and nitrogen was 0.08% - 1.32% , and the content of three monomer units was 0.08% - 1.32% . The precision of the method was 0.72% - 8.22% , and the recovery rate of the method was 90.7% - 114.8% . The precision and recovery rate of the method are good. It can quickly determine the content of each monomer unit in ABS plastics, and provide technical support for the property identification of related imported plastic solid waste.

1. Introduction

Imported recycled plastic is the product under the background of banning the entry of "foreign waste" plastics. Traders purchase the waste plastic produced in developed countries, which is cleaned, sorted, melted and granulated in Southeast Asia and other developing countries and then transported to China for sale. The quality of these imported recycled plastics is often uneven, and the source is very complex. Many of them are just the simple primary processing products of waste plastics without any quality control. Some of them may come from the domestic plastic wastes that are not enough sorted or cleaned, the waste plastics that degrade seriously after being used for many times, or even the medical plastic wastes that carry high-risk substances. These low-end and low-quality recycled plastics imported into China will pose a serious threat to the national ecological environment and people's health. It must be strictly regulated as a ban on the import of solid waste. How to identify the solid waste Characteristic of imported recycled plastics is the key to prohibit the entry of "foreign waste".

ABS is the abbreviation of acrylonitrile-butadiene-styrene copolymer [1-3], which is one of the commonly used engineering plastics. It synthesizes the Characteristic of three components, among which acrylonitrile has high hardness and strength, heat resistance and corrosion resistance; butadiene has impact resistance and toughness; styrene has high surface gloss, easy colouring and easy processing. Characteristics of the above three components make ABS plastics a kind of thermoplastic with the good comprehensive characteristic of “strong quality, tough property and high rigidity”. Adjusting the proportion of ABS three components, the performance also changes to meet the
requirements of various applications, so the composition of the three components in the source unstable recycled ABS may also be quite different. It causes the recycled ABS performance does not meet the national standard requirements.

For the composition of ABS monomer unit, there is no relevant standard for testing. Wang Jian [4-5] and others used Instrumental to only determine the nitrogen content in the ABS and calculated the acrylonitrile content. Zhang Dongfeng [6] et al. determined the content of three monomer units in ABS by pyrolysis gas chromatography, but only analyzed the standard sample, which was not suitable for the complex composition of recycled ABS. Wu Lijun et al. [7] analyzed the blending ratio of ABS/PC materials by near-infrared spectroscopy. Conventional infrared spectroscopy FTIR method needs to analyze the composition of the absorption peaks of specific functional groups, which is difficult to be applied to the recycled ABS plastics; because the ABS plastics are amorphous polymers, and there is no melting process, only glass transition. It is difficult to analyze the composition by differential scanning calorimetry (DSC), and other methods have not been reported.

Under the action of composite catalyst, the Instrumental generates nitrogen, nitrogen oxide, carbon dioxide, sulfur dioxide and water through high-temperature oxidation and combustion of the sample, and enters the separation and detection unit under the promotion of carrier gas. After the non nitrogen compounds are adsorbed on the adsorption column, the oxides of nitrogen are reduced to nitrogen and determined by the detector. The oxides of other elements are determined by adsorption desorption column according to the order of carbon, hydrogen and nitrogen. The standards of Instrumental method are GB/T 30733-2014 (Determination of total carbon, hydrogen and nitrogen content in coal-Instrumental method) [8], GB/T 19143-2017 (Analytical method of element of carbon, hydrogen, oxygen and nitrogen in rock organics) [9], NB/SH/T 0656-2017 (Standard test methods for Instrumental of carbon, hydrogen, and nitrogen in petroleum products and lubricants) [10], etc. The scope of application is respectively organic matter in coal and rock, petroleum products, which are not suitable for the detection of recycled plastics. Therefore, it is necessary to study the method suitable for the analysis of recycled ABS.

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); Multifuge X1R High-speed Centrifuge (Thermo, USA); XP205 analytical balance (Mettler Toledo, Switzerland).

Reagents: Chloroform (Spectral Purity, Shanghai Reagent I Plant).

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

2.2. Operational

2.2.1. Infrared spectrum analysis, the instrument analysis conditions are: ATR transmission, wave-number: 400-4000 cm\(^{-1}\), scanning times >16, confirm whether the main components of the sample is acrylonitrile-butadiene-styrene copolymer.

2.2.2. Differential scanning calorimetry analysis was carried out under the following conditions: programmed temperature rise: initial 20\(^{\circ}\)C, temperature rise to 320\(^{\circ}\)C at the speed of 20\(^{\circ}\)C per minute, hold for 5 minutes, then cool to 20\(^{\circ}\)C at the speed of 20\(^{\circ}\)C per minute, hold for 5 minutes, then temperature rise to 320\(^{\circ}\)C at the speed of 20\(^{\circ}\)C per minute, hold for 5 minutes, nitrogen atmosphere, flow rate of 50ml/min, weighing amount of 2-5mg. The glass transition temperature of the sample is ABS plastic between 95\(^{\circ}\)C and 110\(^{\circ}\)C, and there is no other melting peak in the second heating process.
If the glass transition temperature of the sample is less than 95 °C, the sample may be SAN; if there is
glass transition temperature above 120 °C, the sample may be ABS/PC alloy.

2.2.3. If the sample is colored, the sample may be modified with carbon black, carbon-white or color
master batch, which will affect the composition test. It needs to be purified by pretreatment. The
sample is dissolved by chloroform, those filler in the sample is removed by high speed centrifugal
precipitation. The clear liquid is obtained, and the polymer in the sample is obtained by drying in the
blast dryer until the solvent volatilizes dry.

2.2.4. The polymer in the sample was tested by a pre-calibrated Instrumental by using standard
samples. The analytical conditions were: high purity helium pressure 0.20 MPa; high purity oxygen
pressure 0.15 MPa; combustion furnace temperature 1050°C, reduction furnace temperature 850°C,
sample volume 5 mg, oxygen passing time 40 seconds.

Based on the hydrocarbon and nitrogen content obtained, the results of the three monomer unit
contents in the formula ABS are calculated by the following formula:

\[ C_A = \frac{53}{14} \times m_N \]  
\[ C_B = 9 \times \left( m_H - \frac{3}{14} m_N - 8C_S \right) \]  
\[ C_S = \frac{104}{96} \times \left( m_C - \frac{36}{14} m_N - 48C_B \right) \]

where
\[ m_N = \text{the percent of nitrogen in the sample, mass%} \],
\[ m_H = \text{the percent of hydrogen in the sample, mass%} \],
\[ m_C = \text{the percent of carbon in the sample, mass%} \],
\[ C_A = \text{the percent of the monomer unit of acrylonitrile in the sample, mass%} \],
\[ C_B = \text{the percent of the monomer unit of butadiene in the sample, mass%} \],
\[ C_S = \text{the percent of the monomer unit of styrene in the sample, mass%} \].

3. Results and discussions

3.1. Influence of different sample quality

The sample quantity of elemental analysis in rock organic matter and petroleum products is generally
0.5 mg-5 mg, while that in coal is 70 mg. Considering that the density of recycled plastics is close to
that of organic matter and petroleum products, the results of hydrocarbon nitrogen of the same sample
at 1-13 mg are investigated, and the contents of three monomer units in the sample are calculated, as
shown in Table 1:

| Item                  | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|-----------------------|------|------|------|------|------|------|------|
| sample quality, mg    | 1.23 | 2.06 | 3.21 | 4.11 | 5.38 | 10.06| 13.11|
| percent of nitrogen, mass% | 6.11 | 5.87 | 5.61 | 5.45 | 5.45 | 5.46 | 5.44 |
| percent of hydrogen, mass% | 85.26| 85.45| 85.45| 85.52| 85.50| 85.51| 85.52|
| percent of carbon, mass% | 5.20 | 6.41 | 7.33 | 7.79 | 8.21 | 8.22 | 8.23 |
| percent of acrylonitrile, mass% | 23.13| 22.22| 21.24| 20.63| 20.63| 20.44| 20.14|
| percent of butadiene, mass% | -51.57| -18.90| 5.67 | 17.82| 29.16| 31.32| 38.61|
| percent of styrene, mass% | 125.11| 94.43| 71.55| 60.32| 49.40| 47.42| 40.66|

The results of carbon, hydrogen and nitrogen content and the contents of three monomer units were
plotted by sample size, respectively. The results are shown in Fig. 1 and Fig. 2.
From the above, we can see that when the sample quantity is less than 5 mg, it may be that the sample quantity is too small, which affects the stability of the test results, and the carbon element and hydrogen element results are too small, resulting that the calculated monomer unit content results are wrong, and after the sample quantity is more than 10 mg, it may cause the carbon element result to be too large because of supersaturated, which affects the hydrogen element and nitrogen element content. Hence, it is more appropriate to choose 5 mg sample quantity.

### 3.2. Influence of different combustion temperatures and times

The different combustion time and different combustion temperature can help the complete combustion of the sample and avoid the production of coking substances to affect the final result, while the ash temperature of ABS plastics is generally 600℃, and the selected 1050℃ can be fully guaranteed. According to the principle of time-temperature equivalence, the proper extension of combustion time can ensure full combustion. Select the same sample, three different combustion times, and the results are shown in Table 2:

| Item                     | 1   | 2   | 3   |
|--------------------------|-----|-----|-----|
| combustion times, s      | 90  | 120 | 150 |
| percent of nitrogen, mass% | 5.42| 5.41| 5.42|
| percent of hydrogen, mass% | 85.73| 85.99| 86.01|
| percent of carbon, mass% | 8.846| 8.824| 8.836|
| percent of acrylonitrile, mass% | 20.52| 20.48| 20.52|
| percent of butadiene, mass% | 45.90| 44.55| 44.82|
| percent of styrene, mass% | 33.54| 35.23| 34.97|

As can be obtained from Table 2, the 90 s combustion has been able to guarantee the complete combustion of the sample, so the 90 s combustion time can be selected.

### 3.3. Precision

A repeat ABS was selected for precision testing, and the results are shown in Table 3:
### Table 3. Precision

| Item                              | 1     | 2     | 3     | 4     | 5     | 6     | 7     | Avg. | RSD  |
|-----------------------------------|-------|-------|-------|-------|-------|-------|-------|------|------|
| percent of nitrogen, mass%        | 5.50  | 5.56  | 5.55  | 5.59  | 5.60  | 5.50  | 5.57  | 5.55 | 0.72%|
| percent of hydrogen, mass%        | 84.55 | 84.66 | 84.53 | 84.62 | 84.67 | 84.67 | 84.71 | 84.63| 0.08%|
| percent of carbon, mass%          | 8.389 | 8.381 | 8.393 | 8.248 | 8.221 | 8.435 | 8.545 | 8.37 | 1.32%|
| percent of acrylonitrile, mass%   | 20.82 | 21.05 | 21.01 | 21.16 | 21.20 | 20.82 | 21.09 | 21.02| 0.72%|
| percent of butadiene, mass%       | 36.18 | 35.91 | 36.45 | 32.40 | 31.32 | 37.26 | 39.96 | 35.64| 8.22%|
| percent of styrene, mass%         | 41.50 | 41.60 | 40.98 | 44.82 | 46.07 | 40.56 | 37.86 | 41.91| 6.54%|

The results show that the repeatability of the carbon, hydrogen and nitrogen element test is good, and the precision of element analysis is less than 2%, and the precision of the monomer unit content calculated from this calculation is between 0.72% and 8.22%, which meets the requirement of 10% precision of conventional chemical test, and the precision of the method is good.

### 3.4. Accuracy

A known composition ABS polymer was used to test the accuracy according to the above method, and the results are shown in Table 4:

| Item                              | Repeat result | Test result | Recovery    |
|-----------------------------------|---------------|-------------|-------------|
| percent of acrylonitrile, mass%   | 21            | 20.6~21.5   | 98.1%~102.4%|
| percent of butadiene, mass%       | 33            | 30.0~37.9   | 90.9%~114.8%|
| percent of styrene, mass%         | 46            | 41.7~49.2   | 90.7%~107.0%|

Recovery was 90.7%~114.8%, and the accuracy of the method was good.

### 3.5. Identification of actual sample

In the middle of 2019, an importing company imported a shipment of recycled particles called acrylonitrile-butadiene-styrene copolymer from Malaysia, which was sent to the laboratory for identification of solid waste characteristic because of the inconsistent colour of the goods.

A sample of light yellow plastic particles, mixed with light gray particles, uniform particle size, the main components of the two particles are acrylonitrile-butadiene-styrene copolymer (ABS), as shown in figure 3:

![Original photo of sample](image1)

(a) Light yellow particles after sorting

(b) Light gray particles after sorting

Fig. 3 Recycled plastic particles of acrylonitrile - butadiene-styrene copolymer

Particles of two different colours were tested separately according to the above method, and the results are shown in Table 5:
Table 5. Test results of two different colour samples.

| Item                        | Light yellow particles | Light gray particles |
|-----------------------------|------------------------|----------------------|
| percent of nitrogen, mass%  | 5.5 5.56 5.53          | 4.18 4.19 4.19       |
| percent of hydrogen, mass%  | 84.55 84.66 84.61      | 80.08 80.25 80.17    |
| percent of carbon, mass%    | 8.389 8.381 8.39       | 9.064 9.052 9.06     |
| percent of acrylonitrile, mass% | 20.82 21.05 20.90   | 15.82 15.86 15.80    |
| percent of butadiene, mass% | 36.18 35.91 36.0       | 64.53 63.72 64.10    |
| percent of styrene, mass%   | 41.50 41.60 41.60      | 13.00 13.91 13.50    |

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. Combined with the results of melt mass-flow rate (MFR), it is comprehensively determined that the sample is a mixture of plastic particles with different colours, components and melt mass-flow rate after processing, which belongs to solid waste.

4. Conclusion
This paper presents a method to detect the content of each component in recycled ABS plastics. By means of infrared spectroscopy and differential scanning calorimetry, the recycled plastics are identified as recycled ABS plastics. After necessary pre-treatment, elements such as hydrocarbon nitrogen are analyzed by Instrumental. The content of each unit in recycled ABS plastics is calculated by hydrocarbon nitrogen content. We confirm the uniformity of the sample by technical means, and provide technical support for solid waste identification of imported recycled ABS plastics.

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