Research on analytical and identification methods for nylon 6 and nylon 66 in rubber products

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Abstract: Nylon 66 and nylon 6 enhance tire structural strength, durability and stability. As synthetic fiber cords, they have excellent wear resistance, tensile strength and corrosion resistance, occupying an important position in tire manufacturing. Different tires use different cords, so a simple method is needed for rapid differentiation between nylon 6 and nylon 66. This paper compares methods including DSC melting point, crystallinity, GCMS and TGA: crystallinity test results deviate significantly from theoretical values; TGA weight loss analysis is easily affected by rubber adhering to cords; DSC melting point analysis is relatively fast (≈30 minutes) but requires complete sample stripping from tire rubber, posing processing challenges; GCMS structural analysis takes 50 minutes, is unaffected by surface rubber, and requires no sample processing. Thus, GCMS is determined as the laboratory method for identifying nylon 6 and nylon 66.

Key words: nylon 6; nylon 66; DSC; TGA; GCMS; identification type

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Nylon is a kind of polyamide thermoplastic resin, also known as nylon. Among them, the two most commonly used polyamides are nylon 6 and nylon 66, which account for about 98% of global production capacity and output. Its greatest characteristic is the presence of a considerable number of amide groups in the molecular chain, and the formation of hydrogen bonds between amide groups endows nylon materials with good mechanical properties, fatigue resistance, and wear resistance. As a high-quality environmentally friendly fiber material, it is widely used in various fields such as clothing, automotive, defense, aerospace, etc. At the same time, due to its good mechanical properties, fatigue resistance, and wear resistance, it is also widely used in harsh environments such as garden tools, engine covers and intake manifolds in the automotive field, electronic component substrates and housings in the electronics field, and bearings and gears in the mechanical field. Nylon 6 is formed by the ring-opening polymerization of caprolactam monomers in a head-to-tail manner, while nylon 66 is formed by the alternating polymerization of hexamethylenediamine and adipic acid. The different monomer raw materials of the two lead to significant differences in their structure and properties: nylon 6 has a monoclinic crystal structure, while nylon 66 has a triclinic crystal structure; the melting points of nylon 6 and nylon 66 are 220 ℃ and 264 ℃ respectively; due to the higher density of hydrogen bonding in nylon 66 compared to nylon 6, the crystallinity of nylon 66 is higher than that of nylon 6.

Currently, the application fields of nylon 6 and nylon 66 are becoming increasingly widespread, making it particularly important to accurately and rapidly identify the two types. Based on the differences in structure and performance between nylon 6 and nylon 66, this paper employs three testing methods: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gas chromatography-mass spectrometry (GCMS) for testing and analysis. The aim is to determine a precise and rapid method for identifying nylon 6 and nylon 66 through melting point, crystallinity, thermal

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stability (decomposition temperature), and monomer structure.

1 Experimental part

1.1 Experimental instruments and equipment

DSC: DSC214, Netzsch Scientific Instruments GmbH, Germany;

GCMS: PY3030D/7890B, Agilent Technologies, USA;

TGA: TGA/DSC1, Mettler Toledo, Switzerland.

1.2 Sample

Nylon 6 and nylon 66 are commercially available;

Four unknown samples (nylon cords peeled off from tires).

1.3 Testing and characterization

Melting point analysis of nylon 6 and nylon 66: Utilize DSC (differential scanning calorimeter) to test the prepared samples of nylon 6 and nylon 66. Based on the measurement principle of the heat flow difference between the substance and the reference material during heating or cooling, analyze the characteristic temperatures of nylon 6 and nylon 66 materials. The test procedure is set at 210~310 ℃, with a heating rate of 10 K/min, and the sample size is 5 mg.

Crystallinity testing of nylon 6 and nylon 66: The principle involves calculating the crystallinity based on the heat released or absorbed during the phase transition of the material during heating. When the material is heated, there is a difference in thermal stability between the crystalline and amorphous regions. The molecules in the crystalline region are arranged tightly, requiring a higher temperature to disrupt their structure. Therefore, the crystallinity of the polymer can be inferred by measuring the heat of fusion. The specific formula is: heat of fusion on DSC × 100% / theoretical enthalpy of 100% crystalline material.

Monomer analysis of nylon 6 and nylon 66: During the experiment, a pyrolysis gas chromatography-mass spectrometer was used for analysis. The sample was cut into pieces and weighed at 2mg, then pyrolyzed at 550℃ with helium as the carrier gas. The components separated by the chromatographic column entered the mass spectrometer and were ionized into charged particles (ions) in the ion source. Under the influence of an electric field and magnetic field, these ions were separated according to their mass-to-charge ratio (m/z), forming a mass spectrum. The mass spectrum provides information on the molecular weight and structure of the compounds, and the types of nylon 6 and nylon 66 can be determined based on the structural formula and molecular weight information.

TGA test of nylon 6 and nylon 66: A temperature rise rate of 10 K/min was adopted, with the temperature increasing from 30℃ to 800℃. Throughout the entire process, N_2 was used as a protective gas. The weight loss curves of nylon 6, nylon 66, and sample 2 (an unknown sample peeled off from a tire) were obtained. The decomposition temperature corresponding to the maximum decomposition rate of the two materials was investigated to determine whether it could serve as a test method for distinguishing between nylon 6 and nylon 66.

2 Results and discussion

2.1 Melting point analysis of nylon 6 and nylon 66

In the field of material identification, accurately identifying material categories is crucial for product performance evaluation and quality control. For tire cord materials, specifying their specific type is one of the key factors in ensuring tire performance and safety. Polyamide 6 (nylon 6) and polyamide 66 (nylon 66), as common tire cord materials, are widely used due to their excellent performance. However, due to their similar appearance, distinguishing between the two can be challenging.

Existing literature reports have shown that due to the different structural compositions of nylon 6 and nylon 66, nylon 6 can only form one hydrogen bond with two carbonamide groups, while the carbonamide groups of nylon 66 are arranged relatively, allowing each functional group to form a hydrogen bond without molecular deformation. The theoretical melting point of nylon 6 is 220 ℃, while that of nylon 66 is 260 ℃, and the significant difference in melting points provides an important physical basis for distinguishing between the two. Based on this, this study selected standard samples of nylon 6 and nylon 66, as well as four unknown sample cords peeled off from tires, for testing and analysis.

Differential scanning calorimetry (DSC) is a kind of commonly used thermal analysis technique that can accurately measure the thermal effect changes of materials during heating or cooling, thereby obtaining key thermal performance parameters such as melting point. By conducting DSC melting

point tests on nylon 6, nylon 66, and four unknown samples, the DSC melting point test graph shown in Figure 1 was obtained.

Based on the analysis of the test results, the melting point of Sample 1 is 219.8 ℃, and that of Sample 4 is 218.1 ℃, which are extremely close to the melting point of nylon 6, 219.4 ℃, with minimal deviation. Meanwhile, the melting point of Sample 2 is 260.5 ℃, and that of Sample 3 is 260.0 ℃, which are almost identical to the melting point of nylon 66, 260.6 ℃. This high degree of melting point matching allows us to basically determine that Samples 1 and 4 are nylon 6, while Samples 2 and 3 are nylon 66.

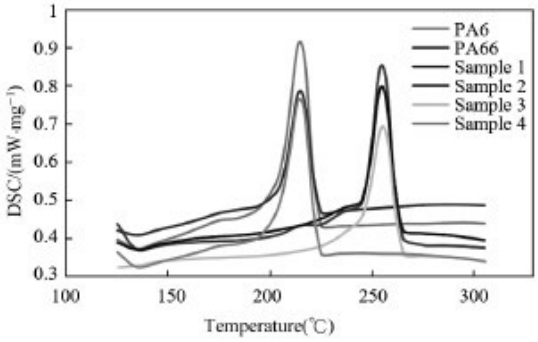

Figure 1 DSC melting point test diagram

2.2 Analysis of crystallinity of nylon 6 and nylon 66

Table 1 Test results of sample crystallinity

project	Crystallinity /%	Project	Crystallinity /%
Nylon 6	23.35	Sample 2	19.63
Nylon 66	31.20	Sample 3	20.99
Sample 1	16.34	Sample 4	21.62

Due to the different hydrogen bond arrangements, nylon 66 exhibits a higher degree of atomic orderliness than nylon 6. The tighter the hydrogen bond arrangement, the higher the crystallinity. Therefore, the crystallinity of nylon 66 is higher than that of nylon 6. As can be clearly seen from the data in Table 1, the crystallinity measured for the four samples obtained from the tires does not match that of the raw materials, nylon 6 and nylon 66. Specifically, the crystallinity of samples 3 and 4 is only slightly higher than that of samples 1 and 2, with minimal difference between them. At the same time, there are deviations in the crystallinity of these four samples from that of the raw materials, nylon 6 and nylon 66, to some extent. Based on such results, it is easy to make misjudgments in practical identification. Therefore, relying solely on crystallinity to identify the type of cord in tires is not feasible.

2.3 GCMS analysis

In the fields of materials science and chemistry, accurately identifying the type and structure of materials is crucial. Gas Chromatography-Mass Spectrometry (GCMS), as a powerful analytical tool, can effectively analyze the molecular structure information of complex mixtures, providing crucial evidence for material research. Polyamide (nylon), as an important type of polymer materials, includes nylon 6 and nylon 66, which are widely used in various industries due to their excellent performance. However, due to the similarity in appearance and some properties between the two, accurate identification poses certain challenges. GCMS technology provides an effective solution for this.

Nylon 6 is formed by the polymerization of caprolactam monomer to produce polyamide, while nylon 66 is formed by the polymerization of hexamethylenediamine and adipic acid. This difference in the monomers used as raw materials forms the basis for identification using GCMS. Through GCMS analysis, different monomers exhibit different retention times in the instrument, resulting in characteristic peaks, which serve as key indicators for distinguishing between nylon 6 and nylon 66.

Based on the mass spectrum results shown in Figures 2 and 3, the retention time of nylon 6, as well as samples 1 and 4, is approximately 33 minutes, which is the characteristic peak of the monomer caprolactam. This peak matches the mass spectrum library, and the matched structure is also caprolactam, indicating that samples 1 and 4 share the same monomer as nylon 6 and can be identified as nylon 6 material or a substance highly related to nylon 6 components. Meanwhile, the retention time of nylon 66, as well as samples 2 and 3, is around 21 minutes, which corresponds to the characteristic peak of the monomer hexamethylenediamine. This peak also matches the mass spectrum library, and the matched structure is hexamethylenediamine, suggesting that samples 2 and 3 can be identified as nylon 66 or contain nylon 66 components.

2.4 TGA analysis

Through TGA analysis of nylon 6, nylon 66, and an unknown sample (sample 2) peeled off from a tire,

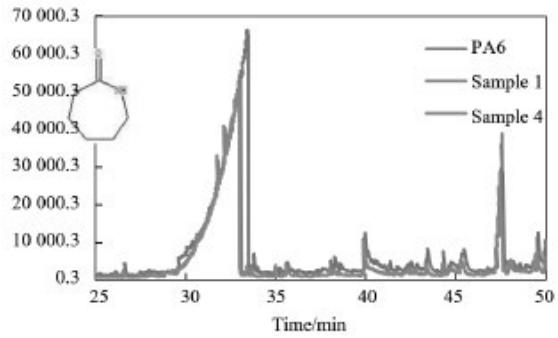

Figure 2 Structural formula and mass spectrum of nylon 6 and its sample

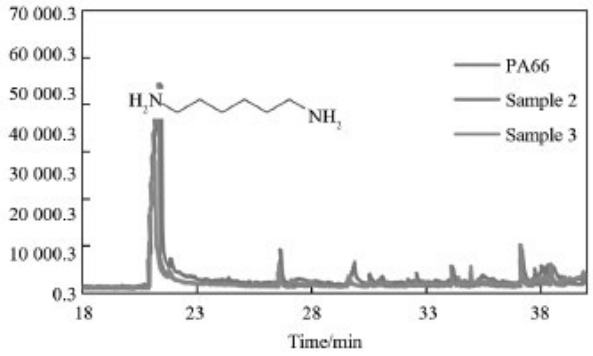

Figure 3 Structural formula and mass spectrum of nylon 66 and its sample

the following conclusions can be drawn: the temperature corresponding to the maximum decomposition rate of nylon 6 is 448.37 ℃, and the temperature corresponding to the maximum decomposition rate of nylon 66 is 430.90 ℃. The temperatures corresponding to the maximum decomposition rates of the two materials are relatively close, indicating that these two materials have certain similarities in terms of thermal stability. However, sample 2 exhibits two decomposition temperatures, with the temperature corresponding to the maximum decomposition rate being 380.28 ℃, which is significantly lower than the temperatures corresponding to the maximum decomposition rates of nylon 6 and nylon 66. This suggests that sample 2 is susceptible to the influence of uncleaned rubber compound on its surface, leading to certain deviations in the results of thermogravimetric analysis. In subsequent research, it is necessary to further optimize the sample surface treatment method to obtain more accurate data on thermal decomposition characteristics, providing accurate data basis for accurately determining the type of nylon in sample 2.

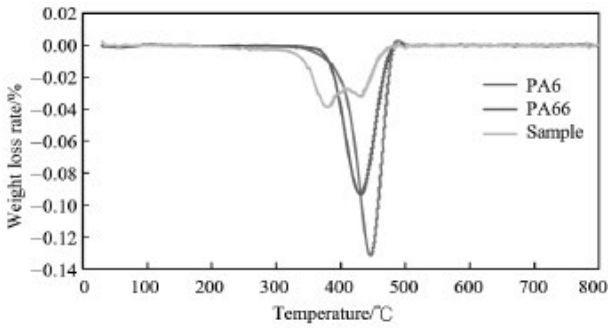

Figure 4 TGA curve of nylon 6/nylon 66/sample

3 Conclusion

According to literature reports, the relative content of blends can be determined by the ATR-FTIR method. The absorption peak position at 1169~1180 cm^{-1} varies significantly with the blending ratio, which can serve as a criterion for component analysis. However, for the testing of nylon cords in rubber, sample preparation is challenging. The rubber compound adhering to the surface of the cord cannot be completely removed, and the presence of rubber compound on the surface can have a certain impact on the infrared testing results.

In summary, relying solely on DSC testing for crystallinity and TGA testing for the temperature corresponding to the maximum decomposition rate to determine the type of nylon is not accurate. Comparatively speaking, using DSC melting point testing combined with GCMS testing to determine the type of nylon yields more reliable results. However, DSC melting point testing has higher requirements for sample processing, as the rubber compound on the sample surface must be thoroughly cleaned, otherwise the rubber adhering to the sample surface will have a corresponding impact on the measured melting point; whereas GCMS testing has lower requirements for samples, and moreover, it can accurately determine the structural formula of nylon cord, thereby accurately identifying the type of nylon cord.

Therefore, based on the above discussion, GCMS qualitative analysis is selected as the most accurate testing and analysis method for identifying the type of nylon cord in this work.