APPLICATION**NOTE**

How Quality Control and Failure Analysis of PP Can Effectively Prevent Scrapping of Goods

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Introduction

Polypropylene (PP) is an often-used raw material for manufacturing thin films like separator films in batteries. This experiment was initiated due to a problem arising during the processing of PP films. Products from certain batches of raw PP granules were easy to break while those from the other batches featured good quality. The objective was to find out the reason behind this, and more importantly, to set up a method for reliable QC of the raw PP granules. Ideally, this QC method would be carried out with a basic DSC or TGA.

Experimental Conditions

Several "good" samples (marked as OK) and "bad" samples (marked as NOK) were collected.

Melting/cooling tests were carried out by means of the DSC 214 *Polyma*. The samples were heated from room temperature (RT) to 200°C at 10 K/min, then cooled down to RT at -10 K/min, followed by a second heating to 200°C at 10 K/min. The testing atmosphere was N_2; the sample sizes were around 10 mg.

OIT tests samples were additionally carried out by means of the DSC 214 *Polyma*. The samples were heated from RT to 200°C in N_2 at 10 K/min, then kept isothermal at 200°C for 5 min. After that, the atmosphere was switched to O_2 (pure) and the time from the switch point to the onset of oxidation was recorded. Sample sizes were around 10 mg.

Pyrolysis tests were done by means of the TG 209 ***F3*** *Tarsus*. The samples were heated from RT to 800°C at 10 K/min in N_2. The sample size was around 10 mg.

Results and Discussion

1. Failure Analysis

1.1. Melting Behavior

As a first step, the melting behavior of all samples was compared to see if there were any impurities, i.e., other polymer components. As shown in figure 1, along with the main melting peak of PP at about 169°C, a small endothermal peak at 148°C can be seen in some DSC curves. This might be due to a second polymer component or additive. However, such a difference cannot be taken as a QC target because this small peak can be found in both the OK and NOK samples.

NGB · Application Note 138 · EN · 0819 · Technical specifications are subject to change.

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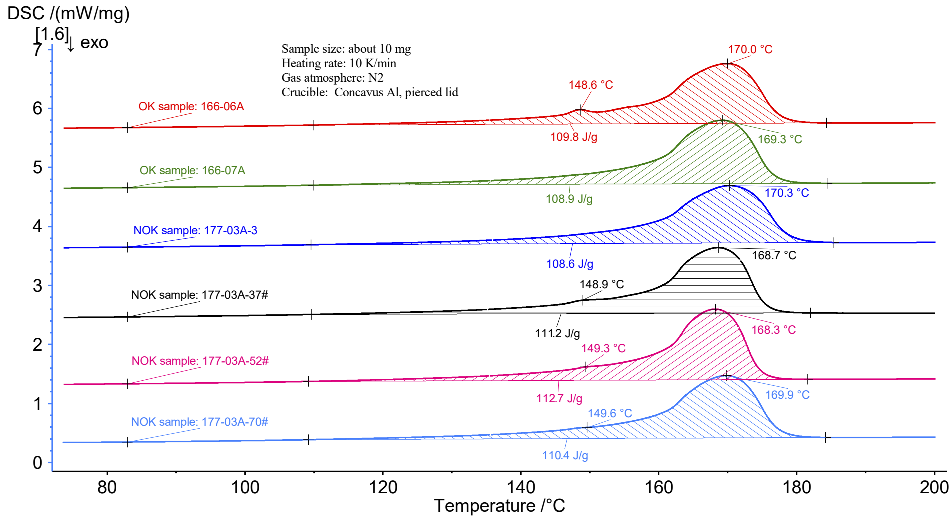
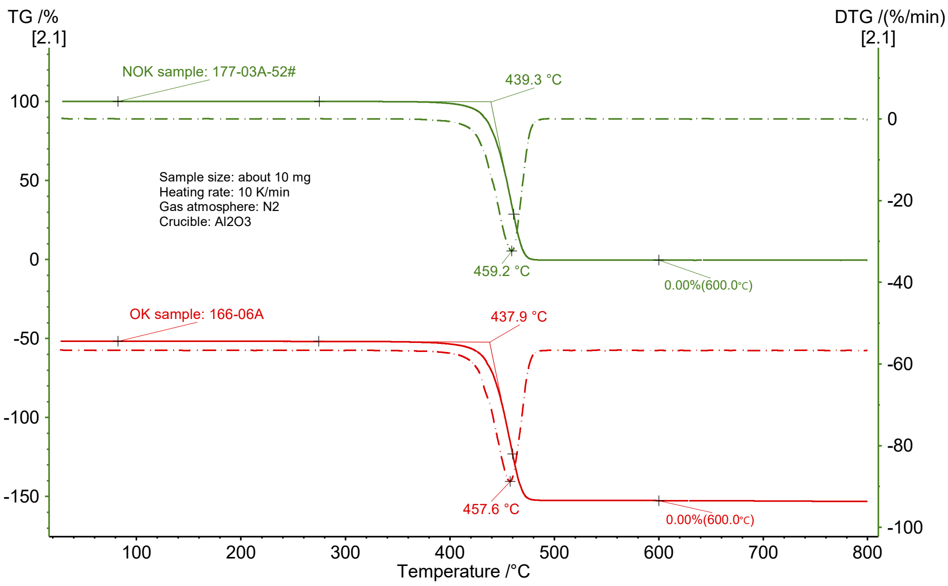


1 Melting (2nd heating) of the OK and NOK samples

1.2. Pyrolysis Behavior

To confirm existence of impurities, the TGA pyrolysis results were compared in figure 2. It seems that both the OK and NOK samples show a weight loss of 100%, and there was no obvious difference between them within the entire pyrolysis procedure.



2 Pyrolysis of the OK and NOK samples

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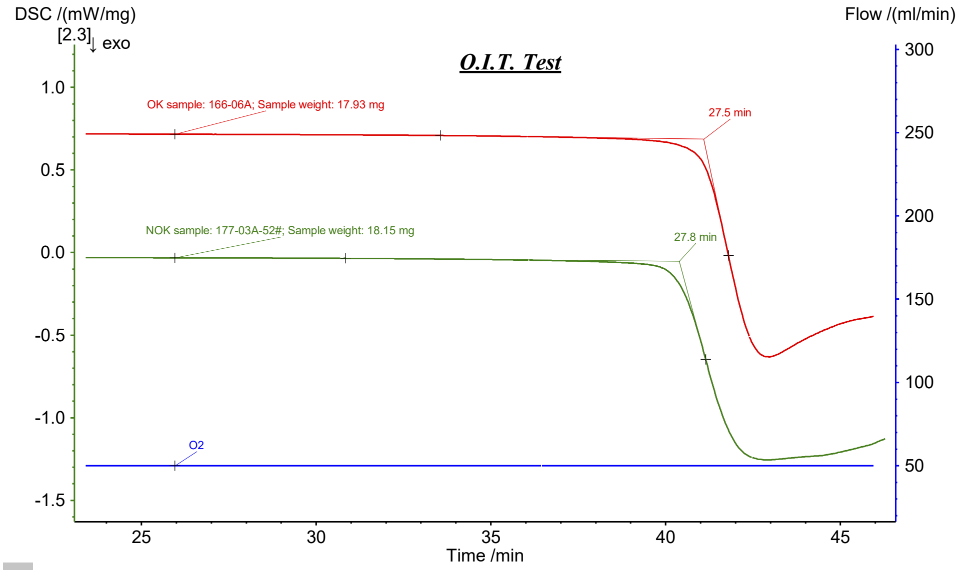


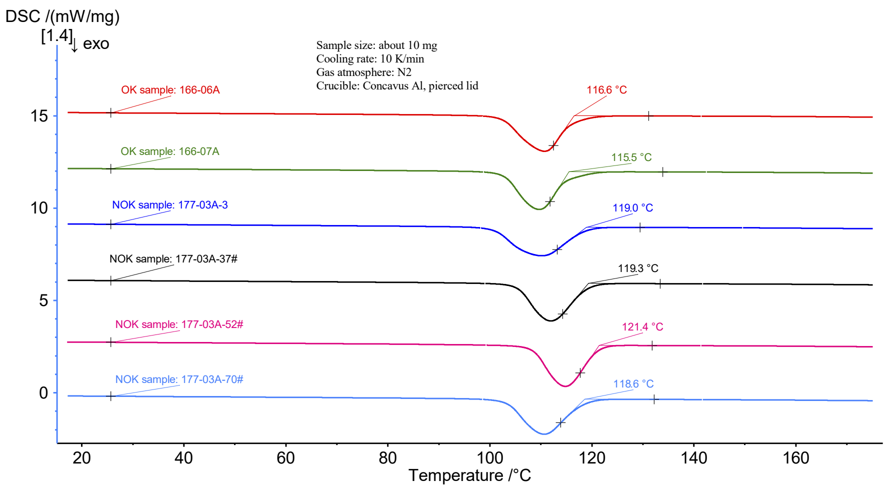
3 OIT test of the OK and NOK samples

1.3. OIT Comparison

"Brittleness" of polymer materials can be a result of differently stabilized materials. Information on the stabilization of a polymer can be distinguished by OIT measurements. Therefore, differing OITs were expected for these samples; such results could then be used as a QC threshold. Unfortunately, as shown in figure 3, there were no significant OIT differences between the OK and NOK samples.

1.4. Crystallization Behavior

The manufacturing process for PP films includes melting of the PP granules followed by the extrusion process. A cooling procedure must have occurred to have induced crystallization. Since the crystallization behavior can also be a factor affecting the quality of the final product, the cooling curves were compared. As shown in figure 4, significant differences in the crystallization behavior between the OK and NOK samples can be seen. Firstly, the onset of crystallization of the OK samples (~115°C) is much lower than that of the NOK samples (~119°C). This means that the NOK samples crystallize more easily. Moreover, the slope of the right side of the DSC peak of the NOK samples appears to be steeper than that of the OK samples. This means that the NOK samples also crystallize faster than the OK samples.



4 Crystallization (cooling) curve of the OK and NOK samples

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1.5. Summary of Failure Analysis

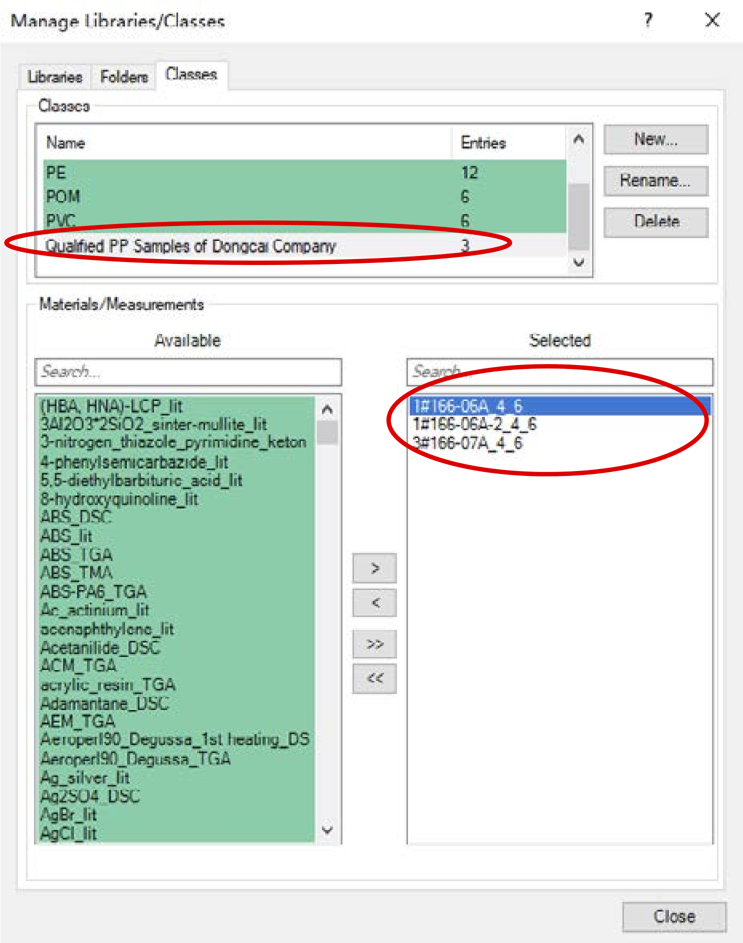
Based on the previous measurements and discussions, we can assume that the "brittle film" problem is probably due to differing crystallization behavior of the raw materials. For raw materials that crystallize more easily (higher onset), or crystallize faster (steeper slope), the product films break more easily. The difference in crystallization may be caused by differing content with regard to nucleation agents, micro-particles, etc.

2. Quality Control Criterion

Based on the conclusion above, the QC criterion can be focused on the crystallization behavior. A simpler solution would be to use the crystallization onset temperature as the QC threshold. This, however, would require manual evaluation (by the operator) and there might be critical issues in the case of "non-ideal" crystallization peaks and baselines. Moreover, the onset temperature cannot reflect the entire situation with regard to crystallization behavior. To compare the crystallization behavior in a more comprehensive way, NETZSCH offers the ideal tool: a solution called *Identify*.

Simply speaking, with *Identify* it is possible to build a database from the cooling curves for the OK samples. The software would then compare these with the cooling curves for the incoming PP granules and could determine whether the incoming PP raw materials are "QC Pass" or "Fail".

For this case, we created a Class in the *Identify* database with the cooling curves for three OK samples. In a real scenario, of course, more curves would be encouraged in order to build a more reliable Class.



5 A Class built from cooling curves of the OK samples

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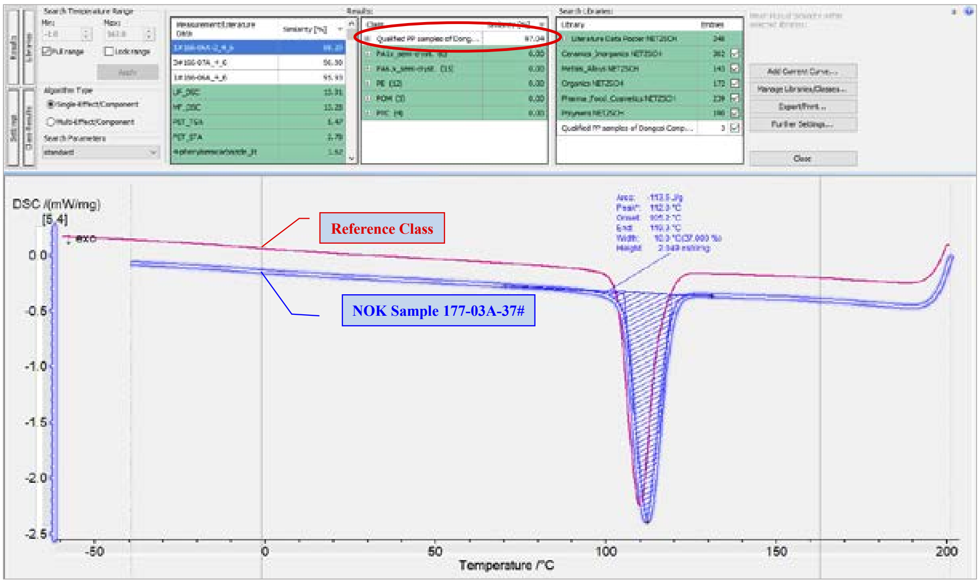
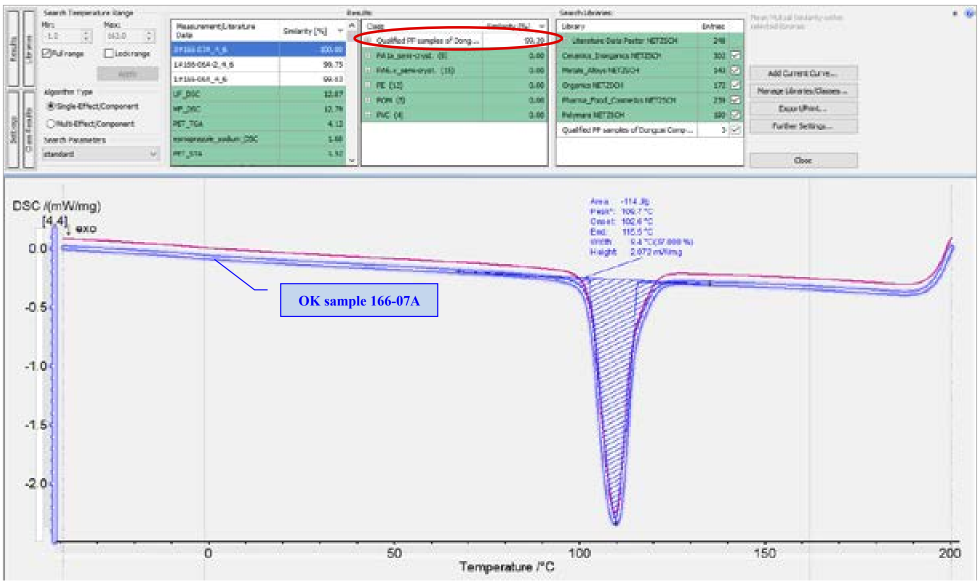
As shown in figures 6 and 7, it is possible to calculate the similarity of the cooling curves for the OK and NOK samples to the Class. For the OK samples, the similarity would be higher than 99% and for the NOK samples, the similarity would be below 99%.

Therefore, it is reasonable to set a similarity threshold at 99%. That is to say, samples can be regarded as a "QC Pass" when the cooling curve has a similarity to the OK Class of higher than 99%. In fact, the *Identify* feature offers a function for running this QC check automatically.



6 Similarity of the NOK samples to the Class



7 Similarity of the OK samples to the Class

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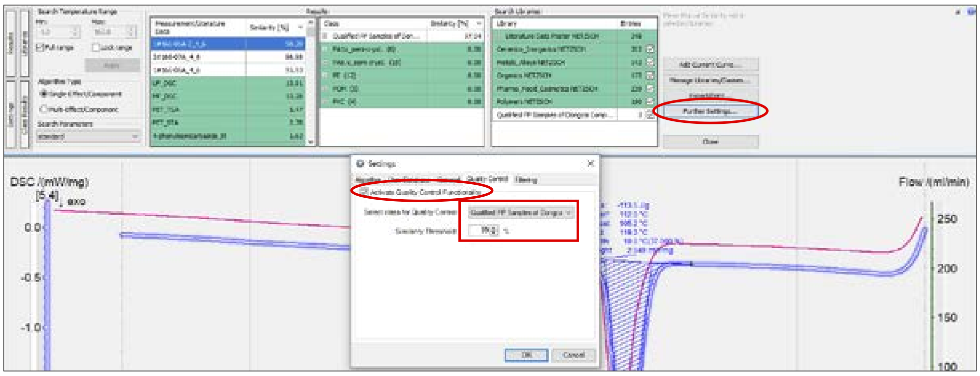
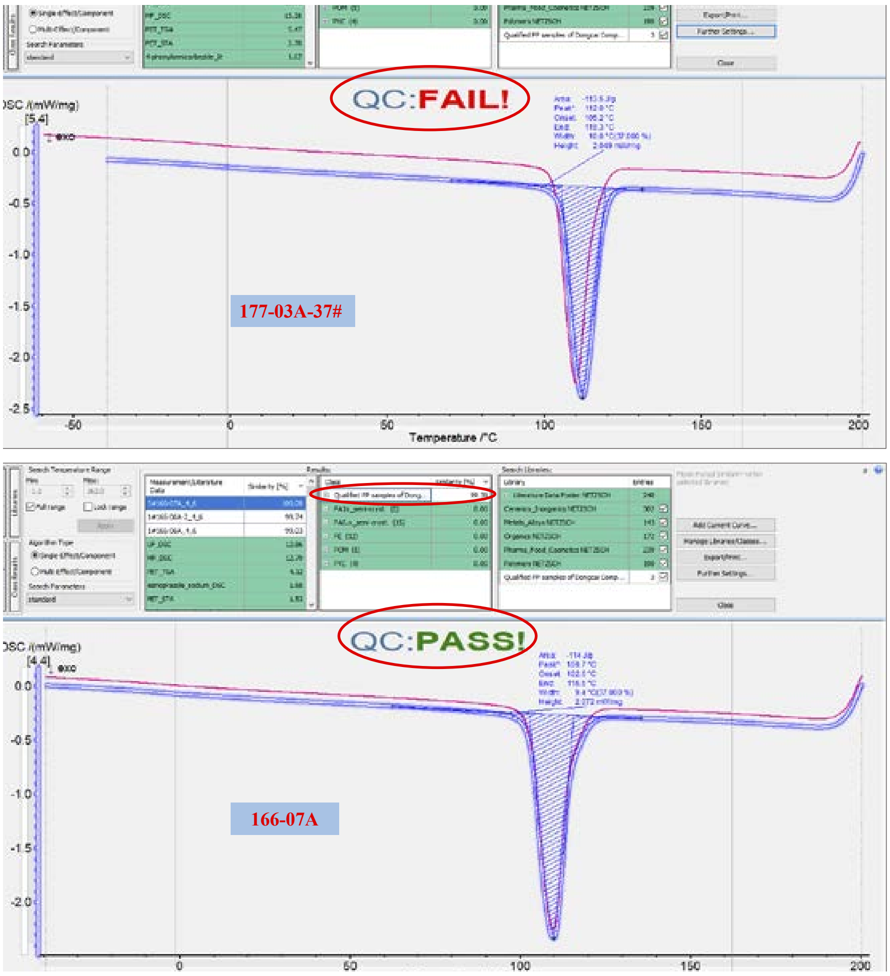
As shown in figure 8, in the "Further settings" window, the user can define a threshold (99% in this case). After that, when a sample's cooling curve is loaded into Proteus® software and *Identify* is triggered, the similarity of the curve to the Class will be calculated, and a QC mark of "FAIL" or "PASS" will automatically appear based on the pre-defined QC threshold (figure 9).



8 Define an appropriate QC threshold (similarity threshold) in *Identify*



9 Automatic QC check via *Identify*

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Conclusion

These test series of DSC and TGA measurements were carried out with the objective of finding the source of failure. It was determined that the quality of the PP films depends on the crystallization behavior of the PP granules.

It is possible to use the crystallization onset temperature of the DSC cooling curve as a simple QC method. However, a more comprehensive and reliable solution can be achieved by applying NETZSCH *Identify* to compare the sample's DSC cooling curve to a reference Class, which can be built from a number of cooling curves for the OK samples. *Identify* can calculate the similarity of the sample curve to the Class and automatically present QC results via a pre-defined QC threshold.

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