APPLICATION**NOTE**

Evaluating the Polymer Ratio in a PET/PC Blend by Means of Modulated DSC

Claire Straßer and Dr. Elena Moukhina

Introduction

Blends consisting of PET and PC exhibit significantly better mechanical properties and processibility than each homopolymer individually. Knowledge of the ratio of each polymer in a PET/PC blend is crucial because it influences the properties of the product.

In this work, modulated differential scanning calorimetry is used to evaluate the amount of each polymer in three PET/PC blends.

DSC Measurements (Conventional)

Experimental

The samples tested consisted of three blends of polycarbonate (PC) and polyethylene terephthalate (PET) in different ratios. They were free of additives or any other component. They were produced in exactly the same way and stored under the same conditions prior to the measurements.

In the following, the three samples are designated PET/PC1, PET/PC2 and PET/PC3.

The measurement conditions are summarized in table 1.

Table 1. Experimental conditions of the conventional DSC measurements

Device	DSC 204 ***F1*** *Phoenix*® (NETZSCH-Gerätebau GmbH)
Atmosphere	Nitrogen (flow rate: 40 ml/min)
Sample masses	Between 11 and 12 mg
Crucible	Cold-welded aluminum crucibles with pierced lids
Temperature program	↗ 0°C ... 280°C at a heating rate of 10 K/min ↓280°C ... 0°C at a heating rate of 20 K/min ↗ 0°C ... 280°C at a heating rate of 10 K/min

NGB · Application Note 234 · EN · 1121 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

NETZSCH

Results and Discussion

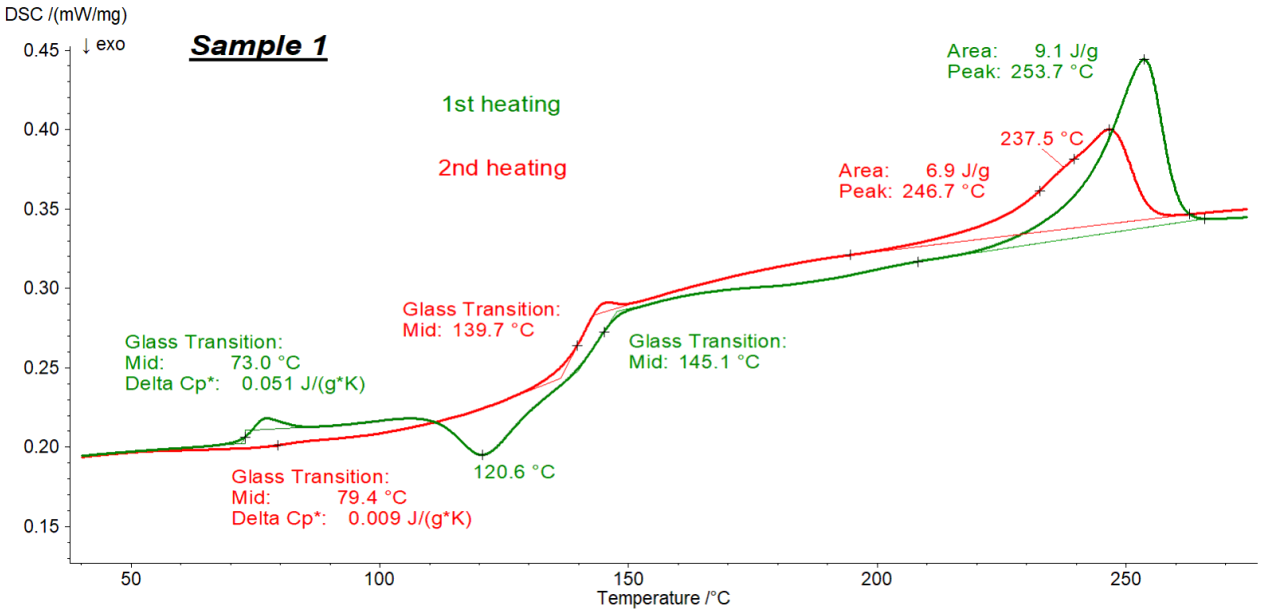
Figures 1, 2 and 3 present the transformation energetics of PET/PC1, PET/PC2 and PET/PC3 during the two heating runs. The first heating run is depicted in green; the second in red.

The DSC curve for the first heating shows the history of the polymer before the measurement: It reflects the preparation, cooling and storage conditions, etc. In contrast with that, the second heating helps identify the polymer. Melting of the polymer in the first heating "erases" its history. After a controlled cooling under defined conditions, the second heating provides information about the identity of the sample.

In both heating cycles for all samples, the typical endothermic step (glass transition) of PET was detected between 70°C and 85°C, along with its melting peak between 200°C and 270°C. For all samples, the Δc_p step of PET was smaller in the second heating than in the first heating, which indicates the formation of a lesser amount of the amorphous phase during cooling. The post-crystallization peak of PET at 120.6°C (peak temperature), only detected in the first heating, confirms this: This effect is due to the reorganization of the amorphous structure to build crystallites and is only detected for low-crystalline PET. The glass transition of polycarbonate is detected at approx. 140-145°C. In the first heating, it overlaps the post-crystallization peak of PET.

Therefore, accurate evaluation of the glass transition of polycarbonate is not possible by means of conventional DSC.

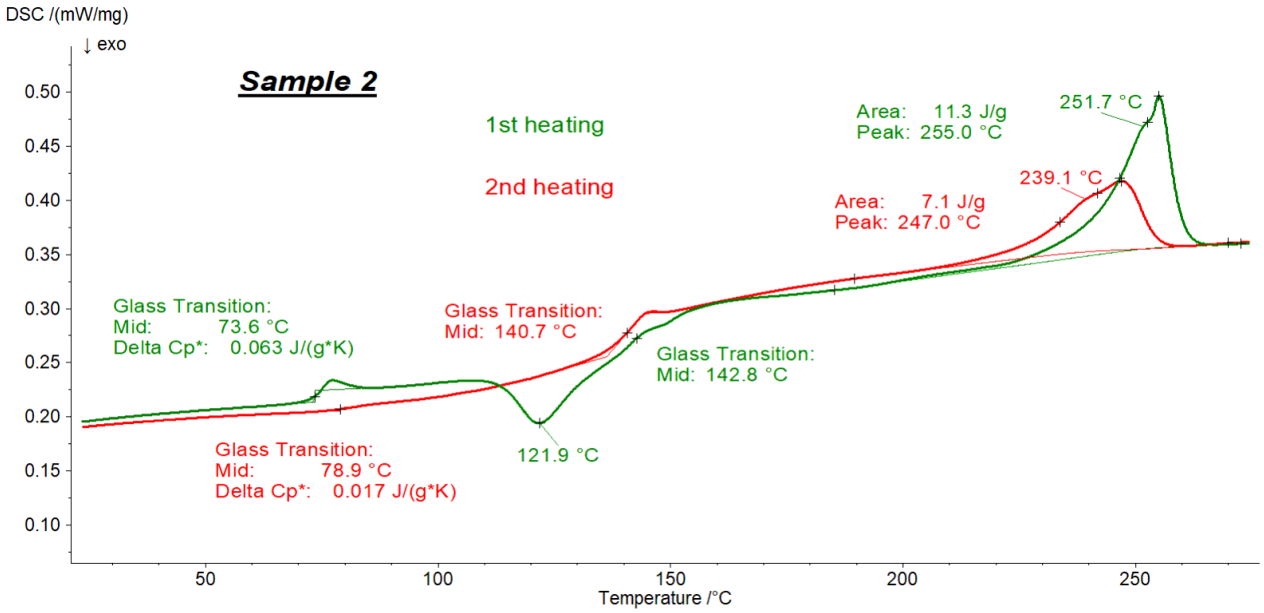
As explained above, the second heating is typically used to identify a polymer substance. However, the polymer ratios are calculated by evaluating the Δc_p inherent to the glass transition. The Δc_p steps of PET in all three cases are higher in the first than in the second heating, so it is more accurate to evaluate them using the first heating. Furthermore, the delivered samples had the same thermal history and were prepared in exactly the same way for the DSC measurements. For these reasons, the first heating was used for evaluating the amount of each polymer in the blends.



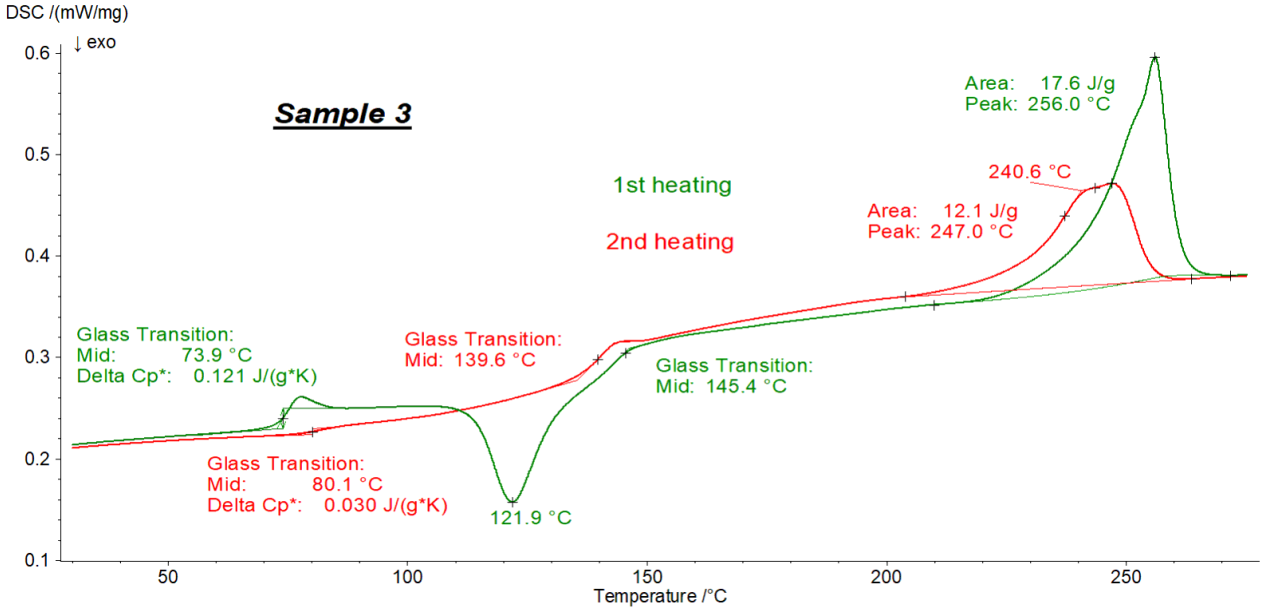
1 DSC Results for sample 1 during the two heating cycles

NGB · Application Note 234 · EN · 1121 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com



2 DSC results for sample 2 during the two heating cycles



3 DSC results for sample 3 during the two heating cycles

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

Temperature-Modulated DSC Measurements

In a modulated DSC measurement, the temperature signal is no longer linear, but sinusoidal: An oscillating heating rate of defined amplitude and period is applied onto the underlying heating rate. As a result, the DSC signal is separated into two parts: the oscillating part, which is the so-called reversing signal giving information about the processes that oscillate with the temperature, e.g., heat capacity changes; and the non-reversing heat flow, which is related to time-dependent processes, e.g., evaporation or crystallization (see also table 2).

Here, temperature-modulated tests are carried out to separate the crystallization peak of PET from the glass transition of PC. This allows for accurate evaluation of the glass transitions.

Experimenal

Table 3 summarizes the conditions for the modulated tests.

Results and Discussion

Figures 4 to 6 present the results of the modulated measurements for the three PET/PC blends. As expected, the glass transition of both polymers is visible in the reversing signal, whereas post-crystallisation of PET can be seen in the non-reversing signal. Furthermore, the endothermic effects after each glass transition, which are due to the relaxation effects of the samples, are also only visible in the non-reversing signal.

It was possible to evaluate Δc_p during the glass transition of the samples with high accuracy in the reversing parts.

Figure 7 shows the reversing signals for all of the samples.

Table 2. Typical distribution of the measured effects into reversing and non-reversing signals

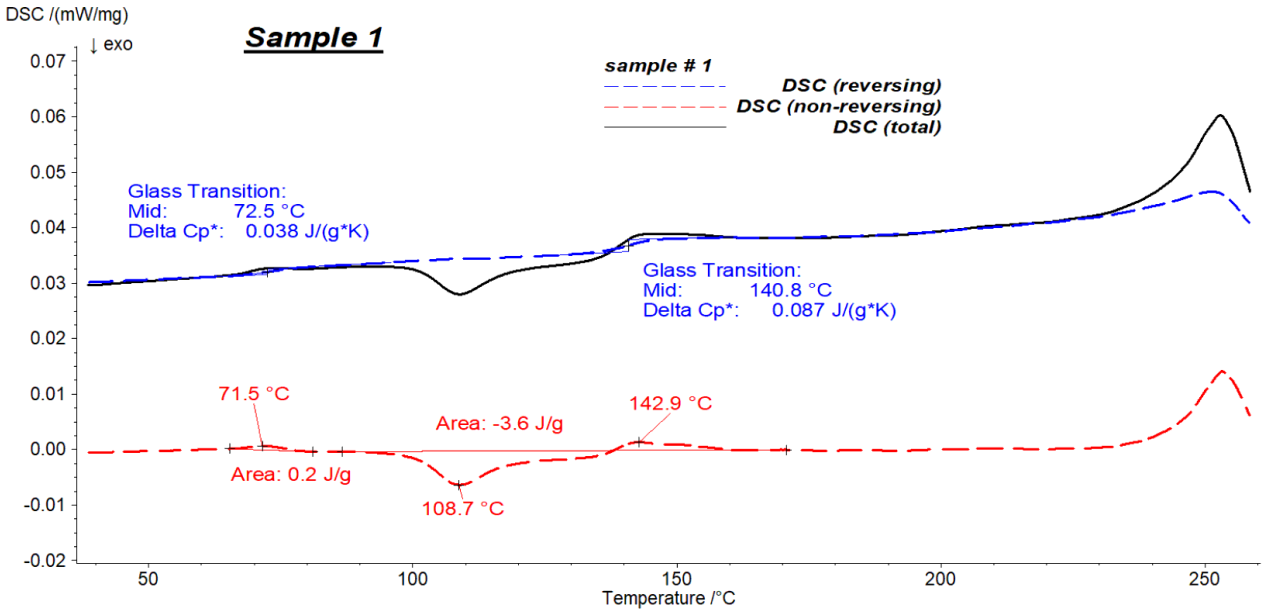
Reversing signal	Non-reversing signal (time-dependent process)
Glass transition	Relaxation
Solid/solid transition	Crystallization, post-crystallizaiton
	Evaporation
	Curing

Table 3. Experimental conditions for the modulated DSC measurements

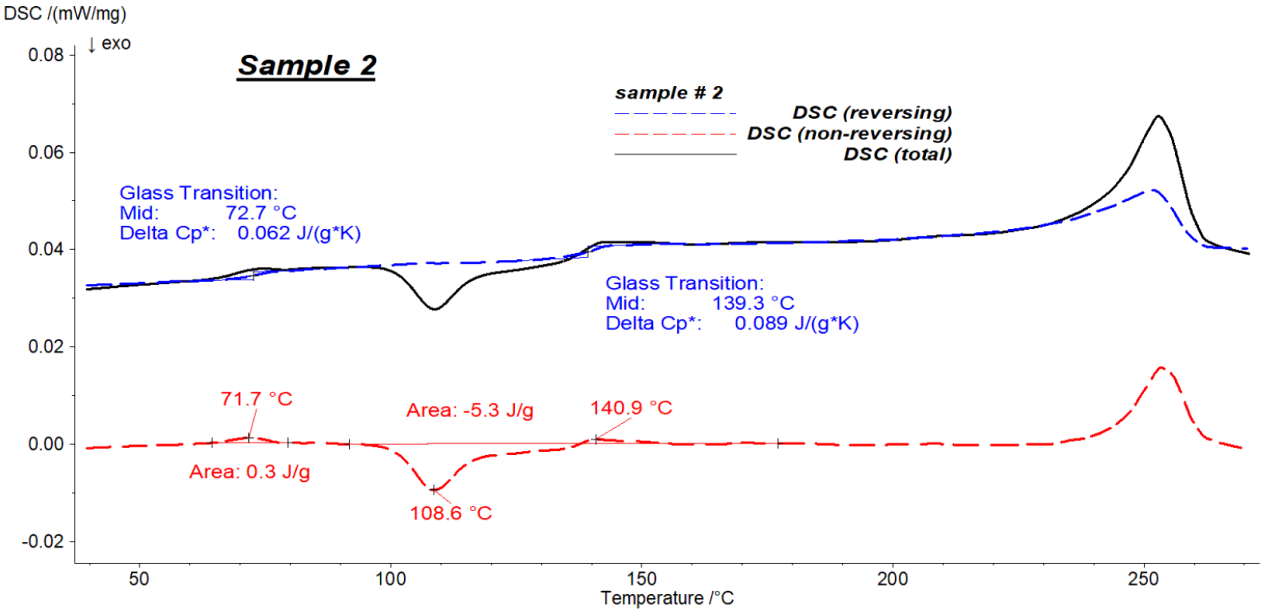
Device	DSC 204 ***F1*** *Phoenix*® (NETZSCH-Gerätebau GmbH)
Atmosphere	Nitrogen (flow rate: 40 ml/min)
Sample masses	between 11 and 12 mg
Crucibles	Aluminum crucibles with pierced lid
Temperature program	20°C - 280°C Heating ate: 1.5 K/min Amplitude: 0.5 K Period: 120 s

NGB · Application Note 234 · EN · 1121 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com



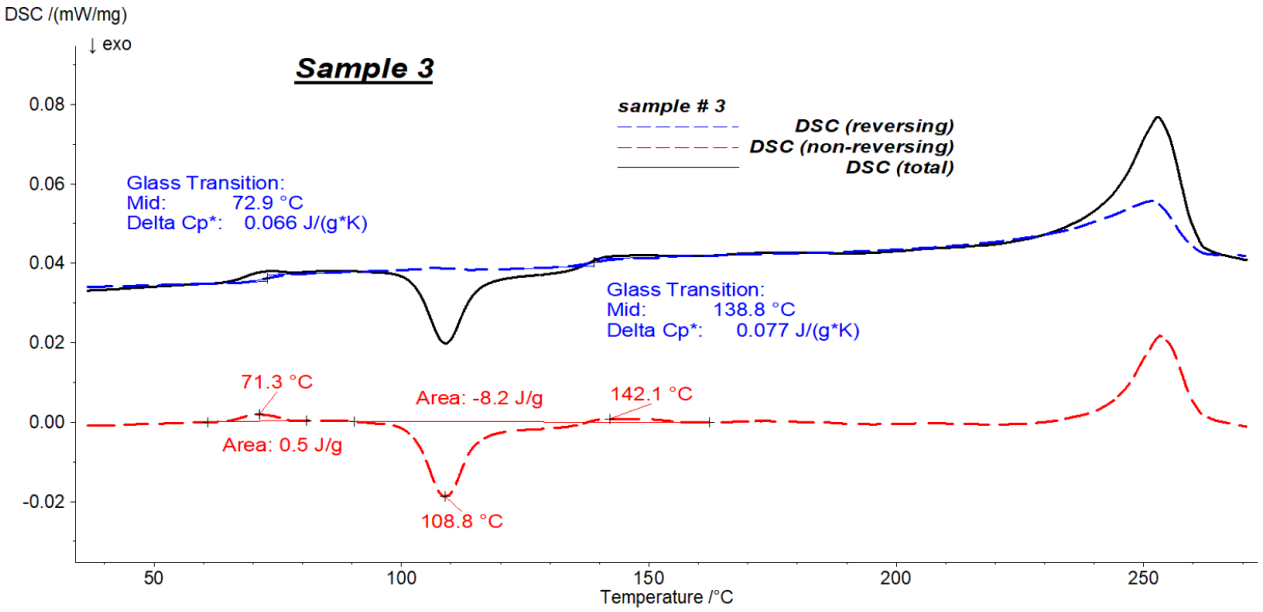
4 Results of modulated DSC measurements on PET/PC1 during the first heating



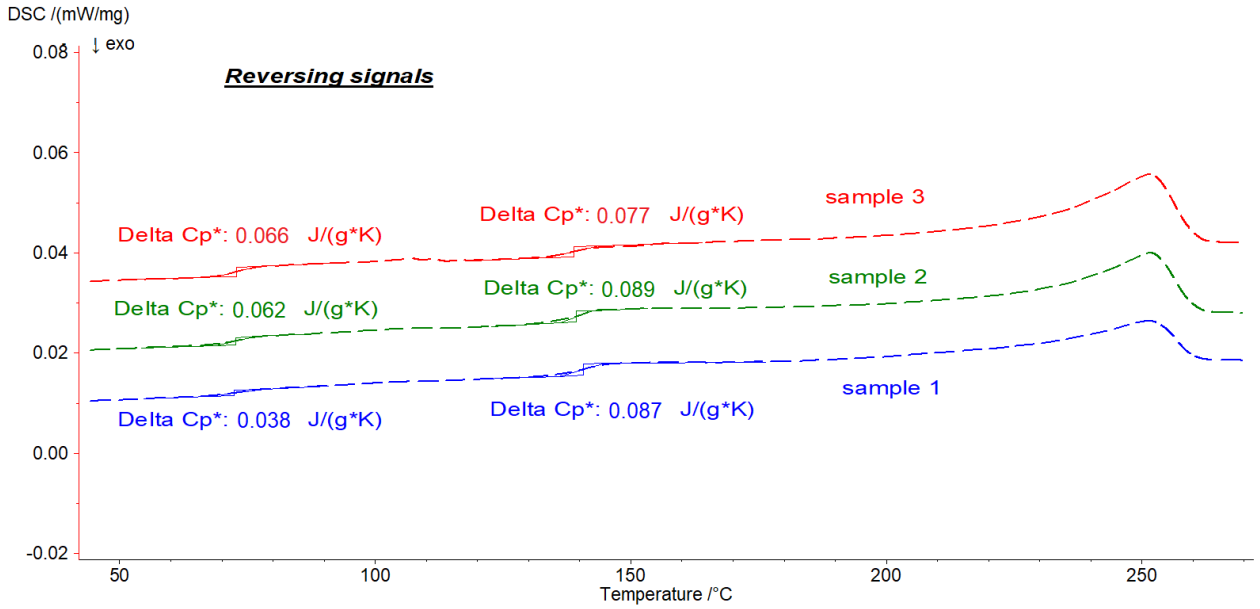
5 Results of modulated DSC measurements on PET/PC2 during the first heating

NGB · Application Note 234 · EN · 1121 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Deutschland
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com



6 Results of modulated DSC measurements on PET/PC3 during the first heating



7 Reversing signals of all samples

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

With this accurate evaluation of Δc_p for the three blends, the amount of PET and PC in each sample can be determined using the followig equations:

$$\begin{cases} \dfrac{PET1}{PET3} = \dfrac{\Delta c_p\,(PETsample1)}{\Delta c_p\,(PETsample3)} \\[2ex] \dfrac{PET2}{PET3} = \dfrac{\Delta c_p\,(PETsample2)}{\Delta c_p\,(PETsample3)} \\[2ex] \dfrac{PC1}{PC3} = \dfrac{\Delta c_p\,(PCsample1)}{\Delta c_p\,(PCsample3)} \\[2ex] PET1 + PC1 = 1 \\ PET2 + PC2 = 1 \\ PET3 + PC3 = 1 \end{cases}$$

in which PET1, PET2, PET3 are the PET content levels in samples 1, 2 and 3; and PC1, PC2 and PC3 are the PC content levels in samples 1, 2 and 3.

These calculations can, of course, only be carried out accurately if the samples include no other component (filler, color batch, etc.) and the thermal history is identical for the three blends.

The following calculations can then be determined:

$$PET1 = \frac{\Delta c_p(PETsample1) \cdot \Delta c_p(PCsample3) - \Delta c_p(PCsample1) \cdot \Delta c_p(PETsample1)}{\Delta c_p(PCsample3) \cdot \Delta c_p(PETsample1) - \Delta c_p(PCsample1) \cdot \Delta c_p(PETsample3)}$$

$$PET2 = PET3 \cdot \frac{\Delta c_p(PETsample2)}{\Delta c_p(PETsample3)}$$

$$PET3 = PET\,1 \cdot \frac{\Delta c_p(PETsample3)}{\Delta c_p(PETsample1)}$$

The values for the Δc_p steps yield the following results:

PET1 = 19.1%	PC1 = 80.9%
PET2 = 23.8%	PC2 = 76.3%
PET3 = 31.3%	PC3 = 68.7%

Conclusion

Three PET/PC blends were measured using the DSC 204 ***F1*** *Phoenix®*. In standard DSC measurements (without modulation), the Δc_p step of polycarbonate is overlapped with the post-crystallization peak of PET; therefore, accurate evaluation is not possible.

Additional measurements were carried out by employing temperature-modulated DSC in order to separate the two effects. The Δc_p steps allow for accurate determination of the content levels of PET and PC in each sample.

NGB · Application Note 234 · EN · 1121 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com