Thermal analysis of toners

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INTRODUCTION

Toners are fine, usually black, powders that are used in modern laser printers and photocopiers. They are in fact complicated mixtures that consist of a thermoplastic base material to which different ingredients such as flowing agents, pigments, UV-stabilizers and other additives have been mixed.

A toner is characterized by the glass transition temperature of its base material and the melting temperatures and melting enthalpies of its additives. These properties can be very easily and reliably characterized by thermal analysis, in particular with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).
This article describes how the two techniques were used to measure a toner sample and compares the results and information obtained. The work was done with a DSC821^e and a DMA/SDTA861^e.

DSC MEASUREMENTS

The sample was first heated at 10 K/min. Afterward it was cooled at 10 K/min and then heated a second time at 10 K/min. The first heating run shows two endothermic peaks that are not completely separated from one another. In addition, a slight shift of the baseline is noticeable. In the cooling curve, several exothermic peaks can be observed that appear shifted to lower temperature in comparison with the heating curve. In addition, a step-shaped displacement of the baseline occurs between 70 °C and 45 °C, i.e. in the same temperature range as the heating run. This indicates that a melting process and a glass transition overlap in the first heating run. In the second heating run of the same sample, only one clear peak is observed. This suggests that the second endothermic peak in the first heating run can be interpreted as an enthalpy relaxation peak that occurs due to enthalpy relaxation in the glassy state on heating (see also UserCom 10, page 13).

This interpretation can be confirmed by heating new samples at different heating rates. Under these conditions the melting peak should be more or less independent of the heating rate, but the enthalpy relaxation should shift to higher temperature with increasing heating rates. The experimental results are displayed in Figure 2. This shows the DSC curves obtained for the first heating runs at heating rates of 0.5, 10 and 150 K/min. The curves show that with increasing heating rates the enthalpy relaxation peak does in fact shift to higher temperatures, but that the melting point is observed at practically unchanged at about 60 °C.

DMA MEASUREMENTS

In dynamic mechanical analysis, a sample is subjected to a periodically changing sinusoidal force. In the linear (Hooke's) region this leads to a sinusoidal deformation of the sample. The deformation is, however, shifted with respect to time in

comparison with the force exerted. The relationship of the force to the deformation amplitude, and the phase shift between the force and the deformation, allow one to draw certain conclusions about the molecular dynamics of the sample. Quantitatively, a dynamic mechanical analyzer yields the storage and loss moduli and the mechanical loss factor (damping).

An important parameter in DMA measurements is the period, i.e. the excitation/oscillation frequency of the sample. The frequency dependence of measurement curves often allows certain effects to be positively identified. For example, crystallization and melting are generally frequency-independent processes. In contrast, relaxation phenomena such as the glass transition are always frequency-dependent. If, in the case of the toner sample, we assume that the measured curve is due to the overlap of a melting process and a glass transition, then it should be possible to distinguish between the two processes through their different frequency behaviour.

The sample was a fine powder. One possibility of measuring materials in powder form in a DMA is to press the powder to a cylindrical disk. The disks are then mounted in the shear clamp of the DMA. Using this technique, we prepared a number of samples from the material with a diameter of 12 mm and a height of 1.5 mm. A pressure of 100 N/cm^2 was used for this purpose.

Figure 3 shows the storage component of the shear modulus of the sample as a function of temperature for frequencies of 1, 10, 100 and 800 Hz. A heating rate of 2 K/min was used. The experiment was performed under displacement control, whereby a displacement amplitude of 1 µm was specified as the set value. The maximum value for the force amplitude was set to 3 N. The curve for 1 Hz shows a broad step in the modulus. With increasing frequency, a second step becomes increasingly apparent. The first step always shows approximately the same starting temperature independent of the frequency. It follows that this step is due to the frequency-independent melting process. The second step, which is clearly visible at high frequencies, corresponds to the glass transition of the thermoplastic constituents in the sample.

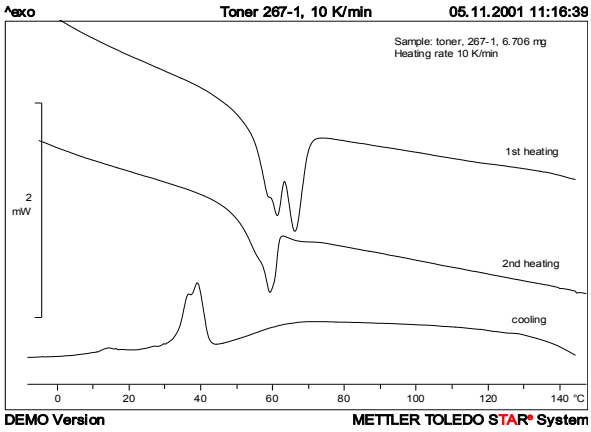

Fig. 1. DSC curves of the first heating run, the cooling run and the second heating run of a toner sample

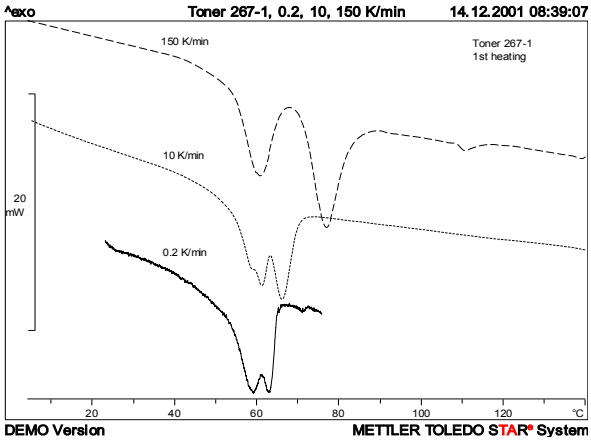

Fig. 2. First heating run of a toner sample at different heating rates.

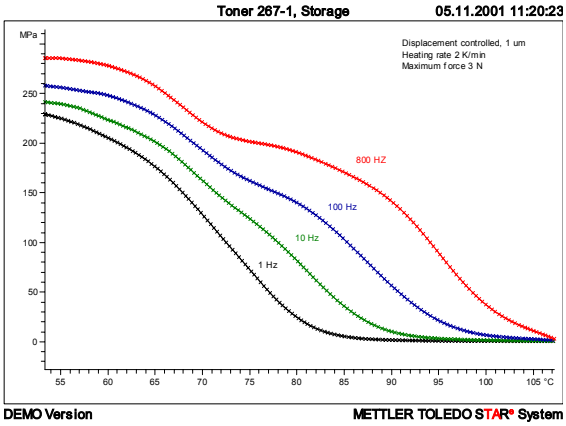

Fig. 3. Storage components of the shear modulus of a toner sample at different frequencies. All 4 curves were measured at 2 K/min.

CONCLUSIONS

Overlapping melting and glass transition processes can be easily separated with both DSC and DMA. In DSC, the fact that the glass transition is dependent on the heating rate is used to separate the two effects. With DMA, the separation is achieved because the frequency dependence of the two effects is different. In principle, both methods yield equivalent results. The sensitivity of the DSC with regard to glass transitions is of course appreciably lower than the sensitivity toward melting processes. The DMA, however, is much more sensitive toward changes in molecular mobility, which occurs in melting processes and glass transitions to the same extent. The wide frequency range of the DMA/SDTA861^e opens up exciting new possibilities for dynamic mechanical analysis.