

## **Crystallization and melting behaviour of plasticized poly(vinylidenechloride)**

### **I. Differential thermal analysis\***

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#### Summary

Poly(vinylidenechloride) powders and films plasticized by different amounts of dibutylsebacate have been investigated by differential thermal analysis (DTA). The molecular mobility of the segments is enhanced by the presence of plasticizer which lowers the glass transition temperature and supports the crystallization behaviour.

#### Introduction

Poly(vinylidenechloride) (PVDC) and its copolymers are semicrystalline polymers which due to their barrier behaviour against water and oxygen are widely applied as packing materials especially in the field of foods. In order to improve the processability and the mechanical properties PVDC is normally compounded with a certain amount of plasticizer. As it is well known the plasticizer influences the glass transition temperature to a great extent, whereas the influence of plasticizer on the crystallization temperature is much less. PVDC belongs to that class of polymers which crystallize poorly and which for that reason are investigated rarely (1).

#### Experimental

The investigated PVDC was a copolymer containing vinylidenechloride (85 %), vinylchloride (12 %), and butylacrylate (3 %). Dibutylsebacate was used as plasticizer in percentages by weight of 3, 5, 7, and 10 %. The investigations were performed with powdery resins (so-called dry-blends) as well as with tubular blown films.

The measurements were carried out using a Mettler TA-2000 equipment within the temperature interval from -50 to 190 °C. The heating and cooling rate was kept constant at 10 K min<sup>-1</sup>. In order to avoid errors caused by condensation the sample chamber was scavenged by gaseous nitrogen. The calculation of the heats of transition was done by a special computer program.

#### Results and discussion

##### Dry blends

The DTA curves of the so-called dry-blends, i.e. plasticized powdery resins, show a nearly disappearing glass transition step at 260 K, a small endothermic peak around 335 K, and a marked double melting peak within the

\* Dedicated to Prof. Dr. G. W. Becker on the occasion of his 60th birthday

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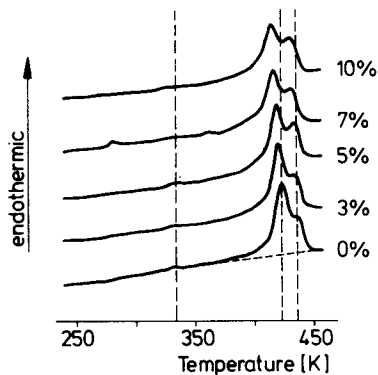


Figure 1: DTA heating curves of PVDC dry-blends. The number refers to the percentage of plasticizer DBS.

temperature interval from 417 to 437 K, as shown in Fig. 1. The maximum of the first melting peak shifts monotonously from 425 to 417 K in dependence on increasing amount of plasticizer, whereas the second melting peak lowers from 437 to 434 K. The measured values of heat of fusion vary between 31 and 35 J/g independently of the plasticizer percentage.

The specimens have been cooled down within the DTA equipment immediately after the first heating cycle; the registered curves are plotted in Fig. 2. The diagrams show a crystallization peak at about 355 K, the area of which increases with growing amount of plasticizer. The measured enthalpy of crystallization during cooling process varies systematically from 0 to 18 J/g.

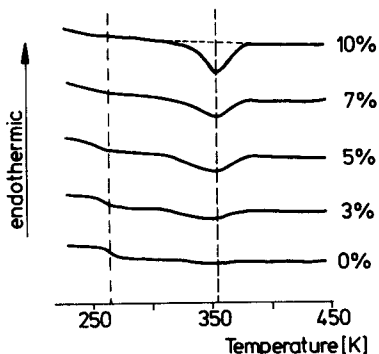


Figure 2: DTA cooling curves of PVDC dry-blends after heating up to 460 K. The number refers to the percentage of plasticizer DBS.

Figure 3 represents the DTA heating curves (2. cycle) following the cooling process reported in the foregoing section. All heating curves show a glass transition step between 250 and 280 K, a crystallization peak with a minimum between 320 and 350 K, and a melting peak with a maximum between 430 and 438 K. As can be seen from the curves in Fig. 3 the glass transi-

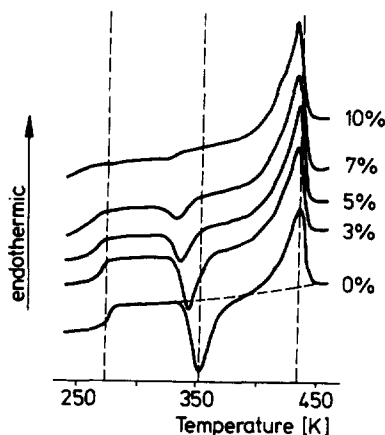


Figure 3: DTA heating curves (2. cycle, see text) of PVDC dry-blends. The number refers to the percentage of plasticizer. The sensitivity is as double as high as in Figs. 1 and 2.

tion temperature as well as the crystallization and melting extrema shift in a systematic way with increasing amount of plasticizer. Moreover, the crystallization enthalpy during the second heating cycle decreases with increasing plasticizer percentage. Obviously those portions of the specimen are now able to crystallize which could not completely crystallize during the preceding cooling due to kinetic reasons, especially in the case of the specimens with low amount of plasticizer.

The heat of fusion of the investigated specimens turns out to be nearly constant at 20 J/g and independent of the percentage of plasticizer. This value is nearly 30 % lower than that of the same specimens during the first heating cycle. Adding the crystallization enthalpies during the cooling and the second heating cycle one gets 18 - 20 J/g for each sample, a value which is equal or a little bit less than the measured heat of fusion. The equivalence between the total crystallization enthalpy and the heat of fu-

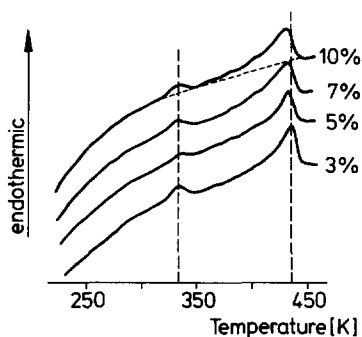


Figure 4: DTA heating curves of PVDC blown tubular films. The number refers to the percentage of plasticizer. The sensitivity is as high as in Figs. 1 and 2.

sion speaks in favour of the quality of the DTA measurements and correctness of the previous statements.

#### Blown tubular films

As mentioned above analogous DTA investigations have been performed with blown tubular PVDC films. The DTA curves which are reproduced in Fig. 4 show a smaller endothermic (melting) peak at about 335 K and a bigger one with a maximum between 431 and 436 K. The heat of fusion amounts to 5 - 7 J/g for the 335 K peak and 25 - 27 J/g for the 435 K peak. The total heat of fusion of all film specimens varies from 31 to 34 J/g; these values are in the same interval as with the dry-blends.

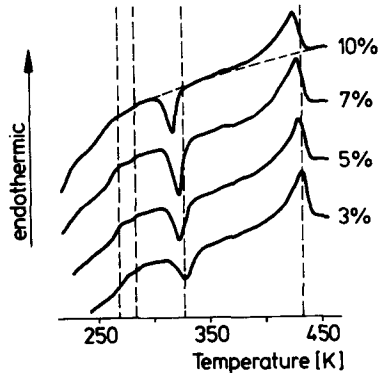


Figure 5: DTA heating curves (2. cycle, see text) of PVDC blown tubular films. The number refers to the percentage of plasticizer. The sensitivity is as high as in Fig. 4.

A second heating cycle has been joined after quenching down the molten films within the DTA equipment very rapidly (cooling velocity 40 - 80 K min<sup>-1</sup>). The respective heating curves are plotted in Fig. 5 which shows a similarity to Fig. 3. Also in this figure the existence of a glass transition process, crystallization phenomenon, and melting process as well as the shift of these events to lower temperature with increasing percentage of plasticizer can be clearly recognized. It should be mentioned that the glass transition step splits into two as marked in Fig. 5: a higher one between 255 and 265 K and a smaller one between 275 and 282 K.

Without presentation of a diagram it will be only notified that a second series of blown films has been investigated which differs from the first one by the cooling velocity during the production of the films. In this case the measured values of the heat of fusion are lowered to 26 - 28 J/g (compared to 31 - 34 J/g for the films of the first series), i.e. the crystallinity decreases with increasing cooling velocity in accordance to what is expected from the point of view of crystallization theory.

#### Influence of plasticizer

As can be clearly seen from the results of the measurements reported above the amount of plasticizer influences the glass transition as well as the crystallization and melting behaviour in a distinct manner. The plasticizer increases the molecular mobility of the segments resulting in a decrease of the glass transition temperature in accordance to the respective

theories (2). On the other hand, the improved segmental mobility gives rise to the enhanced crystallization behaviour during cooling down from the melt (see e.g. Fig. 2). At constant cooling rate the crystallization process makes the more progress the higher the percentage of plasticizer. This behaviour is similar to the so-called liquid inducing crystallization which is well known with poly(ethyleneterephthalate) and poly(carbonate) (3). The influence of the plasticizer on the melting point is minor but nevertheless well observable by DTA (see e.g. Figs. 1, 3 and 4).

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