

## THERMAL STUDIES ON MELTING AND CRYSTALLIZATION OF POLYAMIDE FIBRES

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Effect of heating rate on melting and crystallization of polyamide fibres has been examined using differential scanning calorimetric (DSC) technique. Peak temperature for melting ( $T_m$ ) and crystallization ( $T_c$ ) get suppressed with the increase in the heating rate which has been explained on the basis of chain orientation. Heat of melting ( $\Delta H_m$ ) and crystallization ( $\Delta H_c$ ) have been measured.  $\Delta H_m$  vs.  $T_m$  shows a nonlinear dependence which has been explained on the basis of entropy change. Quantitative difference in  $\Delta H_m$  and  $\Delta H_c$  values has been explained on the basis of orientation and degradation of the polymer.

That the heating rate affects the positions of the DTA/DSC peaks is well known. Schwenker and Zuccarello [1], using a DTA technique, studied the effect of the heating rate ( $3.0$  to  $10^\circ \text{ min}^{-1}$ ) on the melting and crystallization of Dacron fibres. They observed that the crystallization temperature increases on increase of the heating rate, but the melting is not much affected. Using a DSC technique, Pope [2] studied the effect of the heating rate ( $10$  and  $80^\circ \text{ min}^{-1}$ ) on the melting of low-density polyethylene crystals. He observed that the peak temperature is depressed by  $5^\circ$  at the higher heating rate, the reorganization process thus being suppressed.

It appears that a systematic study on the effects of the heating rate on the crystallization and melting processes has not been performed. Thus, a clearer understanding of the effects of the heating rate on the melting and crystallization is needed and this forms the main objective of the present work.

Another intriguing observation is the fact that the heats of fusion and crystallization are not the same; the former is always higher. This difference has in the past been attributed to the fact that the polymer reorients during crystallization. The polymer may also degrade during the melting process, and this may therefore reduce the enthalpy during the crystallization process. This dilemma would also be clarified in the present work.

### Experimental

Nylon-6 (polyamide) fibres of different draw ratios ( $\lambda = 0, 2, 5, 7$  and  $8$ ) were obtained from the Hungarian Viscosa Factory, Nyergesújfalu. The fibres were cut into small pieces with fine scissors before being used in the experiments. Curves

Table 1

 $\Delta n_a$ ,  $T_m$ ,  $T_k$ ,  $\Delta H_M$  and  $\Delta H_K$  values of

$\lambda n_a \times 10^{-8}$		$T_m, T_k, K$					
		$\Phi = 5$		$\Phi = 10$		$\Phi = 20$	
		$T_m$	$T_k$	$T_m$	$T_k$	$T_m$	$T_k$
0	0	482.1	469.4	481.4	464.4	478.9	460.4
2	30.32	484.6	468.9	482.2	465.9	479.8	465.2
5	51.12	487.3	469.9	485.9	466.9	483.1	462.8
7	52.39	487.6	470.4	486.7	467.4	483.3	464.4
8	54.67	487.6	469.7	485.6	467.8	485.9	464.2

 $\Phi$  = heating rate in degree  $\text{min}^{-1}$      $\Delta n_a$  = birefringence

were obtained on a Perkin-Elmer (Model-2B) Differential Scanning Calorimeter (DSC). The setting of the instrument was carried out according to the manufacturer's instructions. The chart recorder was also checked before use. The temperature axis was calibrated under the scanning mode, using the prescribed standard tin sample. All studies were carried out at ambient pressure and under dry  $\text{N}_2$  atmosphere. Weighing was done on a Mettler (Model M5) microbalance.

Aluminium open pans were used in the present studies. The sample was evenly distributed at the bottom of the pan before sealing. About 5 mg sample was used in each run. Scanning operations were performed at 5, 10, 20, 40 and 80  $\text{K} \cdot \text{min}^{-1}$ . Both heating and cooling modes were used in the temperature range 310–520 K. Since it is known that keeping the melt around or above 470 K greatly affects the crystallization, the cooling operation was carried out immediately after the temperature reached 520 K during the heating process. Suitable range settings of 2, 5, 10 and 20  $\text{mcal sec}^{-1}$  for full-scale deflection were used.

The areas under the peaks were measured with a planimeter and the enthalpy changes were calculated by comparing with the area for a standard indium sample of known weight.

Birefringence ( $\Delta n_a$ ) measurements were carried out with a conventional optical method.

### Results and discussion

Typical melting and crystallization curves are shown in Fig. 1. The melting point ( $T_m$ ), peak temperature during melting ( $T_{m,p}$ ), crystallization temperature ( $T_k$ ) and peak temperature for crystallization ( $T_{k,p}$ ) are depicted in Fig. 1.  $T_{m,i}$  and  $T_{k,i}$  are the temperatures for the inception of melting and crystallization, respectively. The data on  $T_{m,i}$ ,  $T_{m,p}$ ,  $T_{m,p}$ ,  $T_{k,i}$ ,  $T_k$  and  $T_{k,p}$  for different fibres are presented in Table 1. It may be seen from Table 1 that all the above temperature points are depressed as the heating rate is increased, thus supporting the observation made

polyamide fibres at different heating rates

$\Phi = 40$		$\Phi = 80$		$\Delta H_m$ , Joules/g	$\Delta H_k$ , Joules/g	$T_m$ at zero heating rate
$T_m$	$T_k$	$T_m$	$T_k$			
473.6	457.9	470.8	448.2	69.5	59.8	481.9
477.1	458.2	474.8	452.7	68.7	61.1	483.4
480.6	460.1	478.8	454.2	72.6	61.3	486.5
481.6	459.9	480.8	454.2	73.8	62.4	486.6
480.1	460.2	480.5	454.2	74.5	63.2	486.9

by Pope [2] on polyethylene crystals. It is a general observation that the temperature of any thermal process shifts forward as the heating rate is increased. This unusual behaviour of the melting and crystallization processes in response to the heating rate may be attributed to the occurrence of some sort of physical orientation, although it is difficult to give an exact explanation at this stage.

The data on the heat of fusion ( $\Delta H_m$ ) and heat of crystallization ( $\Delta H_k$ ) are presented in Table 2.  $\Delta H_m$  and  $\Delta H_k$  are the average values obtained at different heating rates. Figures 2 and 3 give the plots of  $T_m$ ,  $\Delta H_m$ , and  $\Delta H_k$  as functions of the amorphous birefringence ( $\Delta n_a$ ). As Figs 2 and 3 show,  $\Delta H_m$ ,  $\Delta H_k$  and  $T_m$  all increase when the value of  $\Delta n_a$  is increased, and the increase becomes more pronounced beyond a draw ratio ( $\lambda$ ) of 2 to 5. These results are similar to those obtained by Sumita *et al.* [3] for polyethylene fibres. They attributed the marked increase of  $\Delta H_m$  and  $T_m$  with  $\Delta n_a$  to the orientation of amorphous chains, and be-

Table 2  
Enthalpy and weight loss data of polyamide fibres

$\lambda$	$\Delta n_a \times 10^3$	$\Delta H_m$ (Cal · g <sup>-1</sup> )	$\Delta H_k$ (cal · g <sup>-1</sup> )	Average weight loss during melting and crystallization at heating rates 5 to 80 K min <sup>-1</sup> , %	Average enthalpy loss during melting and crystallization at heating rates 5 to 80 K min <sup>-1</sup> , %
0	0	16.61	14.29	4.0	14.0
2	30.32	16.42	14.60	2.9	11.0
5	51.12	17.35	14.65	3.2	15.6
7	52.39	17.64	14.91	3.1	15.5
8	54.67	17.81	15.11	3.3	15.2
				Mean value = 3.3%	Mean value = 14.3%

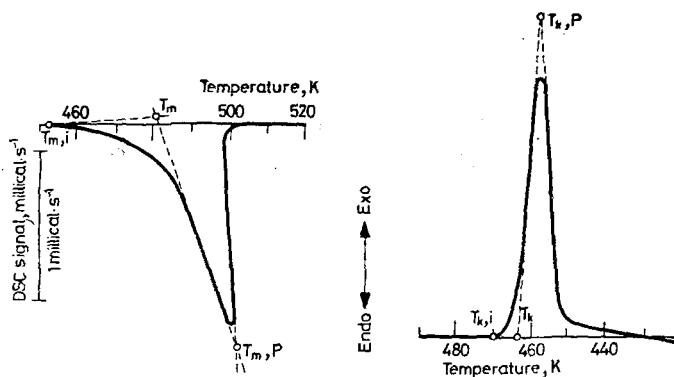


Fig. 1. Melting and crystallization curves of polyamide fiber: Sample:  $\lambda = 0$ ; Heating rate:  $10 \text{ degree} \cdot \text{min}^{-1}$ ; Weight of sample: 5046 mg

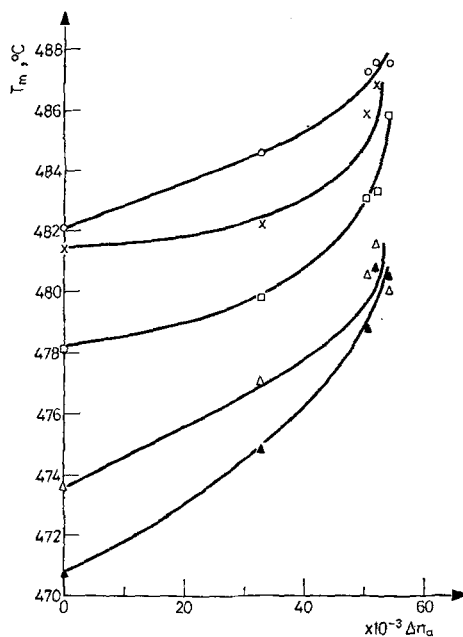


Fig. 2. Dependence of  $T_m$  on  $\Delta n_a$  Heating rate:  $5 \text{ degree} \cdot \text{min}^{-1}$  ○;  $10 \text{ degree} \cdot \text{min}^{-1}$  ×;  $20 \text{ degree} \cdot \text{min}^{-1}$  □;  $40 \text{ degree} \cdot \text{min}^{-1}$  △;  $80 \text{ degree} \cdot \text{min}^{-1}$  ▲

lieve that the crystalline orientation is completed at about the point where marked changes appear in the curves, as is obtained in Figs 2 and 3. A similar explanation perhaps also holds in the present investigation on polyamide fibres.

Figure 4 gives the plot of  $T_m$  vs.  $\Delta H_m$  for different fibres, which shows a non-linear dependence between them. Sumita *et al.* [3] obtained a linear dependence

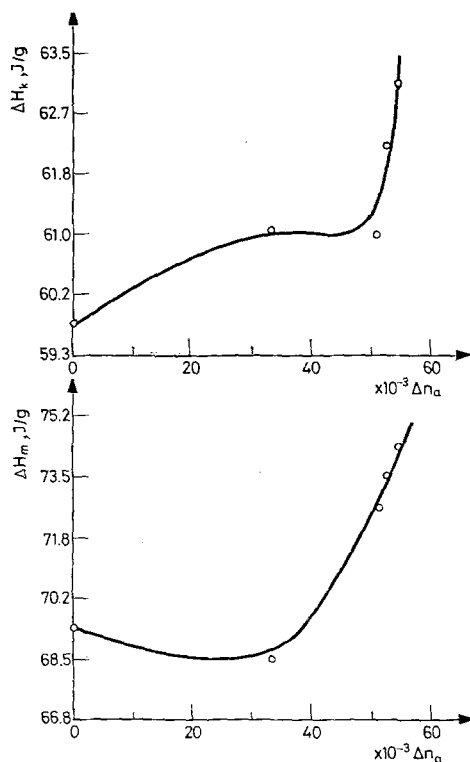


Fig. 3. Dependence of  $\Delta H_m$  and  $\Delta H_k$  on the amorphous birefringence of the fibres. Error in  $\Delta H$  values: 3–5%

between  $T_m$  and  $\Delta H_m$  for polyethylene fibres and gave a mathematical justification for this [3]. If  $T_m$  and  $\Delta H_m$  are linearly dependent on each other, it amounts to the fact that

$$\Delta s = \frac{\Delta H_m}{T_m}.$$

According to this relationship, the entropy change during the melting process for all the samples (having different crystallinity) should remain the same, which is hard to believe. One would therefore expect a non-linear dependence between  $\Delta H_m$  and  $T_m$ , as has been obtained in the present investigation. The correlation between  $\Delta H_k$  and  $T_k$  was also examined in the present work, but it did not follow the trend of  $\Delta H_m$  vs.  $T_m$ , and no other sensible trend was observed either. This shows that the processes of melting and crystallization are quite different from each other. It is expected that such a difference lies in both the thermodynamic and kinetic parameters during the melting and crystallization processes. A sharp difference between  $\Delta H_m$  and  $\Delta H_k$  (Table 2) points in this direction. Further, a

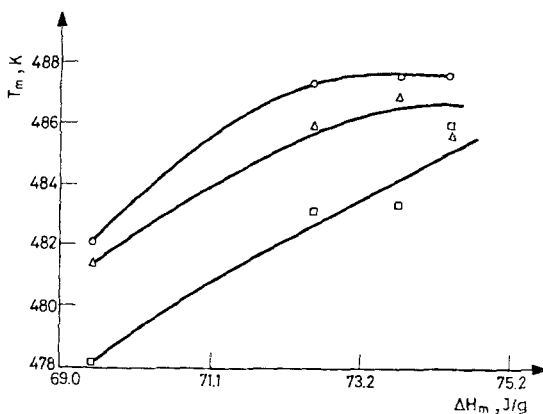


Fig. 4. Dependence of  $\Delta H_m$  on  $T_m$ .  $\circ$  5 degree  $\cdot$  min $^{-1}$ ;  $\triangle$  10 degree  $\cdot$  min $^{-1}$ ;  $\square$  20 degree  $\cdot$  min $^{-1}$

considerable degree of hysteresis has also been observed during the melting and crystallisation in the present work.

The difference between  $\Delta H_m$  and  $\Delta H_k$  has in the past been attributed to the change in the orientation during the crystallization. In the present investigation the weight loss during the melting and crystallization processes was examined. The data on the weight loss and enthalpy changes are listed in Table 2. It may be seen that a quite significant weight loss occurs during the melting and crystallization; this can only be due to degradation during melting and crystallization. Accordingly,

$$\Delta H_{\text{total}} = \Delta H_{\text{degradation}} + \Delta H_{\text{orientation}}$$

From the above relationship the enthalpy change due to the orientation during the melting and crystallization emerges as  $\sim 11\%$ , whereas the apparent enthalpy change is about  $14\%$ .

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### References

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ZUSAMMENFASSUNG — Der Einfluss der Aufheizgeschwindigkeit auf das Schmelzen und die Kristallisation von Polyamidfasern wurde unter Anwendung der Differential-Scanning-Calorimetrie (DSC) untersucht. Die Peaktemperatur für das Schmelzen ( $T_m$ ) und die Kristallisation ( $T_k$ ) wird mit steigender Aufheizgeschwindigkeit herabgesetzt, was anhand der Kettenorientierung erklärt wurde. Die Schmelzwärme ( $\Delta H_m$ ) und die Kristallisationswärme ( $\Delta H_k$ ) wurden gemessen. Die Funktion  $\Delta H_m - T_m$  zeigt eine nichtlineare Abhängigkeit, welche durch die Entropieänderung erklärt wurde. Die quantitativen Unterschiede der  $\Delta H_m - \Delta H_k$ -Werte wurden auf Grundlage einer Orientierung und des Abbaus des Polymers erklärt.

Резюме — С помощью дифференциальной сканирующей калориметрии было исследовано влияние скорости нагрева на плавление и кристаллизацию полиамидных волокон. Температурный пик плавления ( $T_m$ ) и кристаллизации ( $T_k$ ) подавляются с увеличением скорости нагрева, что было объяснено ориентацией полимерной цепи. Измерены теплота плавления ( $\Delta H_m$ ) и теплота кристаллизации ( $\Delta H_k$ ). График в координатах  $\Delta H_m - T_m$  показал нелинейную зависимость, что объяснено изменением энтропии. Количественное различие между  $\Delta H_m$  и  $\Delta H_k$  объяснено исходя из ориентации полимера и его распада.