

Plastic deformation of polypropylene

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(Received 5 March 1985)

The heats of fusion of drawn polypropylene at different draw temperatures (ranging from 22°C–140°C) and draw rates (ranging from 0.05 cm min⁻¹ to 50 cm min⁻¹) were determined to establish the plastic deformation mechanism of polypropylene. At draw ratio $\lambda=6$ and a draw rate $R_d=0.5$ cm min⁻¹ the heat of fusion of drawn polypropylene is a unique function of the draw temperature and is completely independent of the crystallinity of the starting material. The heat of fusion does not change with increased draw rate on drawing at 22°C, but decreases with draw rate on drawing at 60°C or higher temperatures. These results may be interpreted by the phase-transition model of plastic deformation of a semicrystalline polymer. During drawing of polypropylene 'mechanical melting' and strained recrystallization take place at the draw temperature and must be very fast. The new structure of drawn polypropylene is solely determined by the draw temperature, with a slight modification. At a T_d of 60°C or higher, and at higher draw rates, as a consequence of the shorter exposure of drawn polypropylene to the draw temperature at these higher rates, crystallization proceeds for a shorter time at T_d and hence results in a smaller increase in crystallinity.

(Keywords: plastic deformation; polypropylene; heat of fusion; drawing)

INTRODUCTION

Polypropylene (PP) is one of the most useful semicrystalline polymers, and as such it is important to understand the plastic deformation mechanism of this material. There are two general types of model which attempt to explain the structural transformation process associated with the plastic deformation of semicrystalline polymers. The currently accepted mechanism is due to Peterlin¹. Briefly, the model assumes that the heat of plastic deformation is sufficient to mobilize the folded-chain blocks, which then reorganize with an observed new long period. The tendency for lamellae to form mosaic blocks allows mobility of 'loosened' folded-chain blocks, which are then drawn from lamellae and incorporated into microfibrils. In contrast, the accepted correlation between the long period and draw temperature, and the relationship between mechanical energy and heat of fusion, led Juska and Harrison to propose another inherently different type of model^{2,3}. They assumed that regions, of a semicrystalline polymer, melt under stress at the draw temperature, allowing a large and sudden extension, followed by recrystallization at the draw temperature. Other structural elements of drawn material have been shown to agree with this strain-induced recrystallization mechanism of microfibril formation. In addition this model has recently been supported by small-angle neutron scattering (SANS) studies of plastic deformation in crystalline polyethylene⁴.

Investigations of drawn PP, using small-angle X-ray scattering, have shown that drawing drastically changes the long period^{5,6}. The new long period is independent of the previous thermal history of the unoriented starting material, or the final draw ratio, and depends only on the draw temperature. The most startling effect is the drastic reduction in long period. If a slowly cooled or annealed

sample with a large initial long period is drawn at a low temperature, e.g. room temperature for PP, then the sample acquires a long period which is only a fraction of that of the starting material. Such a transformation is completely different from annealing effects in which the long period always increases as a consequence of the tendency of polymer crystals to reduce the surface-to-volume ratio. Peterlin⁷ has proposed that the heat generated during the destruction of lamellae in the bulk sample cannot be removed fast enough. This heat brings about a large amount of chain mobilization in the blocks so that they rearrange with a new long period corresponding to, or determined by, the true temperature of drawing. The true temperature of drawing is presumably related to the sum of the draw temperature (T_d) and a temperature rise (ΔT) caused by the extension energy. In contrast, Juska and Harrison consider that at the draw temperature the strain energies are sufficient to randomize chains, and as a result strained recrystallization occurs. The crystalline state or specifically the crystallinity in drawn PP, as measured for example by heat of fusion, is formed at the draw temperature.

Heat is liberated during the plastic deformation of semicrystalline polymers⁸; variations in the draw rate can drastically change the temperature of the neck region. If the thermally induced mobilization mechanism were true, then the temperature rise of the neck region should presumably influence the heat of fusion of drawn PP. In contrast if the 'mechanical melting' mechanism of Juska and Harrison is correct then there should be little influence of the temperature rise in the neck on the heat of fusion. In the former case, the neck temperature plays a major role in determining the mobility of the sample and therefore, it can be presumed, the final structure of the drawn material. In the recently proposed 'mechanical melting' mechanism, the temperature rise of the neck is the

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direct result of heat loss on recrystallization of an already transforming volume element.

In the work presented in this paper, the heat of fusion of drawn PP was measured at different draw temperatures and different draw rates. Particular attention was given to the relationship of the heat of fusion to the draw rate.

EXPERIMENTAL

An isotactic polypropylene film PP5225 (Shell Development Co.) was used. The heat of fusion of the starting material is 20.5 cal g^{-1} . Samples of polypropylene with different heats of fusion were prepared as follows. A film of starting material was pressed between two aluminium sheets at 176°C for 10 min. The film was then annealed at different temperatures for various times or quenched in ice water. The heats of fusion of the unoriented starting materials are 17.5, 20.5, 22.8, 23.8 and 24.6 cal g^{-1} respectively. Annealing was performed in a thermostatically controlled hot-air oven.

The films were cut into strips of the usual dumbbell shape (drawing region $14 \times 3 \text{ mm}$ —ASTM D638-V). Drawing was carried out using an Instron model 1102 instrument; the desired drawing temperature was achieved using a thermostatically controlled hot-air oven.

The sample was clamped in the oven for 10 min to reach thermal equilibrium, and was then drawn at different rates, from 0.05 cm min^{-1} to 50 cm min^{-1} . The draw ratio in the neck was determined from the displacement of ink marks made on the sample before deformation and separated from each other by constant intervals. Immediately after drawing, the film was removed from the oven, and allowed to cool at room temperature before the heat of fusion was measured.

Thermal measurements were carried out on a Perkin-Elmer differential scanning calorimeter (DSC-2) with data station (TADS). For all experiments the sample size was kept nearly constant at approximately 5 mg. A fixed scan rate of $20^\circ\text{C min}^{-1}$ was used for the melting thermogram, and the temperature scale and energy response were calibrated with indium. The average value of ΔH_f for three samples of each particular type is reported, the range for any three sample set was approximately 0.2 cal g^{-1} .

RESULTS AND DISCUSSION

Heat of fusion

The morphological aspects of drawn PP have been investigated by electron microscopy, wide- and small-angle X-ray scattering and other methods⁹, but a systematic study of the heat of fusion (i.e. crystallinity) of drawn PP has not previously been undertaken.

The experimental results on heats of fusion obtained for PP samples drawn at different temperatures and as a function of thermal history are summarized in Figure 1. The ordinate $(\Delta H_f)_d$ represents the heat of fusion of drawn PP and the abscissa $(\Delta H_f)_0$ is the heat of fusion of the undrawn starting PP. The draw rate was 0.5 cm min^{-1} , the draw ratio varied between 5 and 6, and draw temperatures ranged from 22°C – 140°C . The experimental results show that there is a marked influence of draw temperature on the heat of fusion. The higher the draw temperature, the larger the heat of fusion. The thermal history of the starting material does not play any detectable role in determining the new heat of fusion. The

drawn PP attains a final heat of fusion which depends exclusively on the draw temperature.

The specific effect of draw temperature on the heat of fusion of drawn PP is shown more clearly in Figure 2. At low T_d the heat of fusion of drawn PP changes more with temperature changes than at higher T_d ; the reverse is true for the normally reported long period changes.

All of these data can be readily explained by the recently proposed stress-activated phase transition model. In the model it is assumed that local strain-energy is sufficient to randomize chains at the draw temperatures. This means that local regions of a sample 'melt' at the draw temperature. Once melting occurs, recrystallization proceeds within a strained melt. Crystallinity in drawn PP is therefore formed at the draw temperature. As a result the heat of fusion of drawn PP is solely a function of the draw temperature and is independent of the previous thermal history of the starting material. As noted earlier, changes in SANS data have been observed during the solid state deformation of polyethylene by Wignall and Wu⁴. These results are consistent with the occurrence of 'melting' and recrystallization during plastic deformation of a semicrystalline polymer.

Heat of fusion as function of draw rate

It is useful to investigate the correlation between the heat of fusion and the draw rate in order to try to understand further the plastic deformation mechanism of

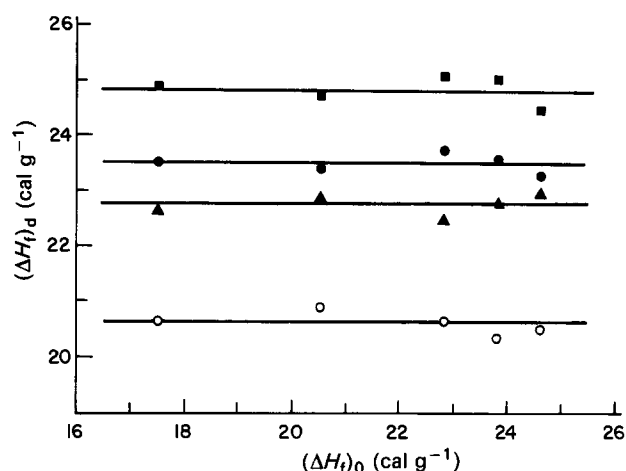


Figure 1 The heat of fusion of drawn PP as a function of heat of fusion for different undrawn starting PP samples. Draw temperature; (○): (22°C); (▲): (60°C); (●): (80°C); (■): (140°C)

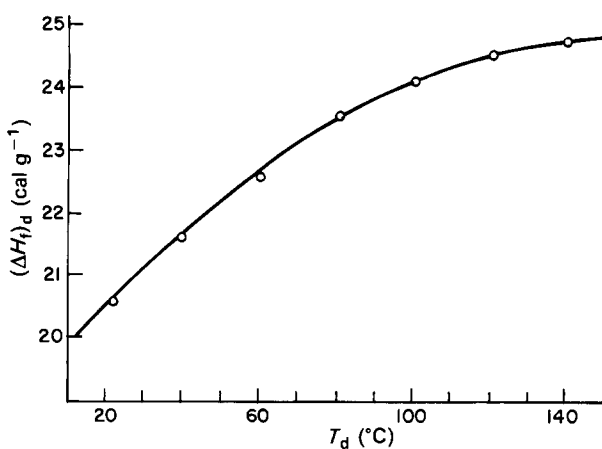


Figure 2 The heat of fusion of drawn PP as a function of draw temperature

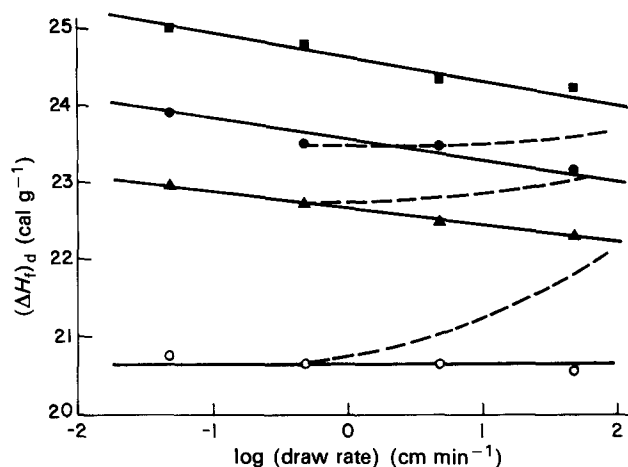


Figure 3 Heat of fusion of PP drawn at different draw rates. (—): experimental results. Draw temperature: (○): (22°C); (▲): (60°C); (●): (80°C); (■): (140°C); (---): the heat of fusion calculated from adiabatic temperature rise

semicrystalline polymers. The effect of draw rate on heat of fusion of drawn PP is plotted in *Figure 3*. In general, at a T_d of 60°C or higher, the heat of fusion decreases with increasing draw rate. At $T_d = 40^\circ\text{C}$ only a small decrease is observed (not shown), and at $T_d = 22^\circ\text{C}$ there is effectively no change in $(\Delta H_f)_d$ with draw rate.

With increasing draw rate there is a shorter time for heat to be removed from the neck, so that the actual temperature in the neck region is higher than the ambient temperature of drawing. According to Peterlin's model this temperature rise imparts additional mobility to the chains in the crystal blocks so that the nature of the crystalline phase is determined by this 'true' temperature of drawing. Peterlin has calculated the adiabatic temperature rise of drawn PP by analysing the true stress-strain curve of a volume element. On the basis of these calculations one would expect that the heat of fusion should increase with draw rate as a consequence of the increasing 'true' temperature of drawing. The dashed lines in *Figure 3* represent the heat of fusion calculated from this temperature rise. What one calculates is opposite to the observed experimental results, and at $T_d = 22^\circ\text{C}$ the greatest discrepancy is observed.

The fact that the heat of fusion is effectively independent of draw rate at $T_d = 22^\circ\text{C}$ shows that the

crystallinity of drawn PP is determined exclusively by the draw temperature. As predicted by the Juska and Harrison phase-transition model, during plastic deformation of a semicrystalline polymer 'mechanical melting' and strained recrystallization take place at the draw temperature and must be very fast.

Experimental results also showed that when a sample drawn at 60°C with a draw rate of 50 cm min⁻¹ was annealed at 60°C for 200 min, its heat of fusion reached that of the sample drawn at 60°C with draw rate of 0.05 cm min⁻¹. Presumably, the faster the draw rate, the shorter the time a drawn region of the sample is exposed to the draw temperature. As a result, heats of fusion of the drawn PP decrease slightly with increasing draw rate.

CONCLUSIONS

1. The percentage crystallinity of polypropylene is determined by the draw temperature, and is not a function of the thermal history of the original undrawn polypropylene.

2. At $T_d = 22^\circ\text{C}$, the heat of fusion of drawn polypropylene is almost independent of draw rate. This result supports the phase-transition model used to describe the plastic deformation of semicrystalline polymers. 'Mechanical melting' and strained recrystallization take place at the draw temperature, and occur rapidly under these particular conditions.

ACKNOWLEDGEMENTS

The authors are pleased to express their appreciation to the Shell Development Co. for its kind support of this research.

REFERENCES

- Peterlin, A. *Polym. Eng. Sci.* 1977, **17**, 183
- Juska, T. and Harrison, I. R. *Polym. Eng. Rev.* 1982, **2**, 13
- Juska, T. and Harrison, I. R. *Polym. Eng. Sci.* 1982, **12**, 766
- Wignall, G. D. and Wu, W. *Polym. Prepr.* 1983, **24**(2), 235
- Balta-Calleja, F. J. and Peterlin, A. *J. Polym. Sci., A-2* 1969, **7**, 1275
- Balta-Calleja, F. J. and Peterlin, A. *J. Mater. Sci.* 1969, **4**, 722
- Balta-Calleja, F. J. and Peterlin, A. *J. Polym. Sci., A-2* 1972, **10**, 1749
- Vincent, P. *Polymer* 1960, **1**, 7
- Peterlin, A. *J. Mater. Sci.* 1971, **6**, 490