Thermal Properties of Drawn Polytetrafluoroethylene

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Synopsis

Polytetrafluoroethylene as polymerized (virgin) was drawn, sintered, and annealed. By thermal analysis the changes in crystal type and crystallinity and melting kinetics was analyzed. It is shown that this analysis permits control and optimization of the various processes. In addition, a new, high melting polytetrafluoroethylene (654 K) is described. It is assumed to be metastable due to strain in the surrounding amorphous fraction.

INTRODUCTION

Polytetrafluoroethylene (PTFE) crystals were found to undergo a transition to a condis crystalline mesophase at about 300 K, i.e., just above room temperature.[1] The resulting condis phase is *con*formationally *dis*ordered and shows conformational mobility.[2] It is thought that the motion consists mainly of conformational (trans +) ↔ (trans −) exchange as is needed for helix reversals.[3] Positional and orientational order of the chains is retained to a similar level as in the low temperature polymorph.[4] The conformational freedom causes the softness of the material, as expected for a mesophase, but the parallel arrangement of the chains results also in a lower shear viscosity[5] than in the isotropic melt, which is stable only at much higher temperature (above about 605 K).

This unique combination of properties of polytetrafluoroethylene has an important practical application, it makes PTFE processible below its isotropization temperature (usually, improperly, called melting temperature). It is of particular interest for ultrahigh molecular mass polymers that were shown to be practically 100% crystalline when crystallized during polymerization.[6] In this paper the properties of PTFE subjected to different mechanical and thermal treatment, as used in industrial applications, are studied. The main goal of this research was to identify crystals melting between 600 and 625 K with a peak at about 618 K, about 10 K above the equilibrium melting

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temperature. In addition, a new endotherm at about 650 K, not described before, will be demonstrated. Thermal analysis is the research tool used throughout.

EXPERIMENTAL

Sample characterization and kinetics experiments were carried out with a Du Pont 990 Thermal Analysis system. The temperature scale and heats of transition were calibrated with high purity standards (anthraquinone, potassium perchloride, lead and zinc).[7] The PTFE studied was originally in form of granules of ultrahigh molecular weight. It was a product of ICI. Its molecular mass was estimated to be above at least 2×10^6. Samples of about 2–10 mg were used for analysis. The standard of heating rate was 10 K/min.

Sample Preparation

The starting material was extruded at 315 K through a cylindrical die in the presence of an inert plasticizing liquid (naphtha) in the form of a cylinder. During this step individual powder particles coalesce by plastic deformation. The plasticizing liquid was then removed at 395 K.

Next, the sample was subjected to an 8:1 drawing step at 572 K at a deformation rate of 1600 %/s. The deformed material has little lateral cohesion and strength and fibrillates easily.

To improve the cohesion, a sintering step was carried out in the temperature range T_s of 600–650 K, i.e., close to and above the equilibrium melting temperature. The sample was kept at T_s for a predetermined period of time. This sintering was followed by air-quenching to room temperature.

For analysis of the processes occurring at T_s, some samples were cooled down to 600 K only, at which the sample is metastable, i.e., it neither melts nor crystallizes. For analysis, the sample equilibrated at 600 K were then heated to complete melting at the standard melting rate of 10 K/min. The heat of fusion that remained after this heat treatment was used as a measure

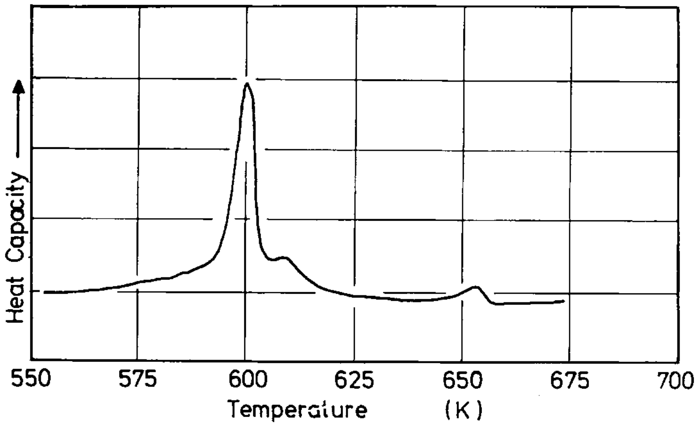

Fig. 1. Typical DSC trace of PTFE subjected to a complete cycle of sample preparation consisting of extruding, drawing, sintering at 615–644 K and cooling slowly to room temperature. Heating rate 10 K/min. Melting peaks: 599.7, 610.3, and 654.5 K. Division of the heat of fusion among these three peaks: 82, 14, and 4%, respectively. Overall heat of fusion 1694 J/(K mol). Crystallinity 41%.

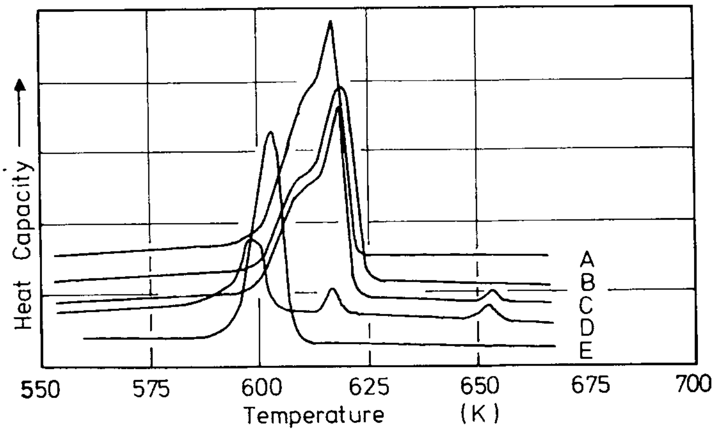

Fig. 2. DSC traces taken at 10 K/min for (A) virgin PTFE, (B) extruded, undrawn, nonsintered sample, (C) extruded, drawn, nonsintered material, (D) partially sintered and recrystallized sample C. After sintering at 612 K for 10 min, the sample was cooled in air by taking it out of the DSC cell. (E) Completely sintered (molten) and recrystallized sample C. Melting at 720 K for 10 min. Cooling conditions were the same as in curve D.

of the progress of sintering (and fusion). As a standard, the heat of fusion of completely crystalline PTFE, 4.10 kJ/mol, was used.[1]

The final step of the analysis is cooling to room temperature. During this process recrystallized structures are formed from the melt.

RESULTS

Overall Analysis

In Figure 1 a typical example of a DSC trace of the material after completion of sample preparation process through steps 1–4 is given. Three endotherms are present, identified by their approximate melting peak temperatures at 600, 610, and 655 K. These and additional melting peaks were characterized by detailed thermal analysis after every step of preparation.

Characterization of the Starting Material

In Figure 2, curve A, a DSC curve taken at 10 K/min for the starting material is shown (before treatment step 1). The sample begins melting at 544 K. The extrapolated onset of melting, which for good crystals is often close to the equilibrium melting temperature, is at 594 K. The peak temperature is 617 K and the end of melting is at 625 K. Peak and end temperature show clear signs of superheating.[8] The main melting peak is preceeded by a low temperature shoulder. We observed such a shoulder also in PTFE samples of different origin.[1] The heat of fusion of samples as shown in Figure 2, curve A, was found to average 4.05 kJ/mol. This value is close to that found previously for material obtained from a different source (4.10 kJ/mol).[1] As a further characterization, the molecular mass was estimated using the heat of crystallization on cooling at 1 K/min as described by Suwa et al.[9] We found this heat of crystallization to be 1.258 kJ/mol, which corresponds to a molecular mass of about 2×10^6, in agreement with the molecular mass suggested by the supplier.

Extruded Material

A DSC trace of dried, extruded, but undrawn product (after step 1) is shown in Figure 2 as curve B. The heat of fusion is within experimental precision not changed from the starting material of curve A. The samples were uniform along their entire lengths and registered heats of fusion of 4.03 and 4.09 kJ/mol for the middle and end of a given sample, respectively. The sample shows some increased superheating at the melting peak (2 K) and a very shallow, high-temperature melting tail that extends to 650 K (1–2% of the total of fusion).

Characterization of Drawn Material

A typical DSC trace of the material after the drawing step 2 is shown in Figure 2, curve C. Superheating of the main melting peak is slightly less than for the extruded material (1 K). The peak temperature is 618 K. The sample is now clearly nonuniform and has a heat of fusion which is considerably less. A sample from the middle of the drawn material had a heat of fusion of 3.06 kJ/mol, while two samples taken from the two ends had heats of fusion of 3.53 and 3.37 kJ/mol, respectively. The characteristic temperatures of fusion changed little along the sample. The high temperature melting tail remained unchanged from the extruded, undrawn material, but between 650 and 658 K, another, new endotherm appears with a peak temperature of about 654 K. The heat of fusion under this peak varies also along the sample (from 100 J/mol in the middle to 52 and 17 J/mol at the two ends, respectively).

Characterization of the Sintered Material

In Figure 2, curve D, an example of the melting of a sample sintered at 612 K for 10 min, followed by quenching to room temperature is shown (after step 3). The melting peaks of the residual drawn PTFE (618 K and 654 K) are clearly evident. In addition, there was some recrystallization on cooling, giving rise to the melting peak at 600 K. Note that neither the position nor the area of the high temperature melting peak (654 K) changed on this treatment.

Curve E in Figure 2, finally, shows a DSC trace of a completely molten PTFE that was subsequently recrystallized. The sample was kept at 720 K for 10 min and then quickly cooled. Although melting begins below 500 K, the majority of the sample melts between 595 and 614 K, with a peak temperatures of 603 K. Evaluation of the heat of fusion (2.39 kJ/mol) and comparison with the starting material leads to a crystallinity of 60%. There are no low or high temperature shoulders on this melting peak.

Analysis of the Kinetics of the Sintering Process

The sintering process is characterized mechanically by a compacting of the sample and increasing cohesion. This is achieved by increasing fusion and recrystallization during cooling. Over 50 DSC curves were run and analyzed, covering kinetics of changes in the crystals melting originally in the temperature range of 600–650 K. The heat of fusion of the residual crystals melting at about 618 K was used as a standard against which the progress was judged. Table I contains these remaining heats of fusion under the 618 K melting peak after sintering for different times at the given temperatures. Table II lists

TABLE I
Heat of Fusion (J/mol) as a Function of Sintering Temperature and Time for the 618 K Main Melting Peak

Sintering time (min) \ Sintering temp (K)	600	603	607	610	611.5	615	618	625	643	644	650
0	4045	4045	4045	4045	4045	4045	4045	4045	4045	4045	4045
1	—[a]	2075	1626	1321	797	176	0	—	—	—	0
2	—	—	—	—	581	—	—	0	—	—	—
3	—	—	—	—	410	—	0	—	—	—	—
5	—	1593	1137	986	209	—	0	—	—	—	0
5.5	—	—	—	—	—	—	—	—	—	0	0
10	—	1522	757	510	57	—	—	0	0	—	—
15	—	—	—	—	—	—	—	—	—	—	0
17	—	—	—	—	—	—	—	—	0	—	—
20	—	—	—	307	25	—	—	—	—	—	—
30	—	938	406	—	33	—	—	—	0	—	0
60	—	—	169	33	—	—	—	—	—	—	0
90	1845	478	82	—	—	—	—	—	—	—	—
120	—	—	69	—	—	—	—	—	—	—	—
180	—	303	—	—	—	—	—	—	—	—	0
360	—	171	32	—	—	—	—	—	0	—	0
720	1425	—	30	—	—	—	—	—	—	—	0
1440	—	—	16	—	—	—	—	—	—	—	—

[a] — indicates that this combination of time and temperature was not measured. The significant figures correspond to average computation and do not indicate the precision that does not exceed ±5%.

TABLE II

Heat of Fusion (J/mol) as a Function of Sintering Temperature and Time for the 654 K Main Melting Peak

Sintering time (min) \ Sintering temp (K)	600	603	607	610	611.5	615	618	625	643	644	650
1	—	91	57	83	85	93	83	—	—	—	60
2	—	—	—	—	85	—	—	73	—	—	—
3	—	—	—	—	104	—	94	—	—	—	—
5	—	87	76	73	98	—	72	95	—	—	70
5.5	—	—	—	—	—	—	—	—	—	61	—
10	—	75	61	84	88	—	—	89	91	—	—
15	—	—	—	—	—	—	—	—	—	—	61
17	—	—	—	—	—	—	—	85	—	—	—
20	—	—	—	116	98	—	—	—	—	—	—
30	—	102	95	—	99	—	—	—	83	—	42
60	—	—	76	89	—	—	—	—	—	—	50
90	75	107	83	—	—	—	—	—	—	—	—
120	—	—	95	—	—	—	—	—	—	—	—
180	—	98	—	—	—	—	—	—	—	—	9
360	—	104	86	—	—	—	—	—	18	—	5
86	69	—	30	—	—	—	—	—	—	—	0
1440	—	97	76	—	—	—	—	—	—	—	—

[a] — indicates that this combination of time and temperature was not measured.

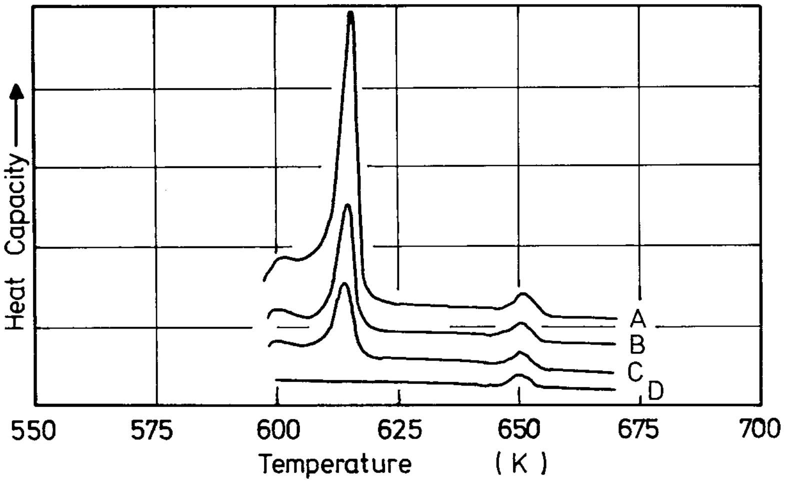

Fig. 3. DSC traces illustrating extruded and drawn samples sintering at 610 K: (A) after 1 min: (B) after 5 min; (C) after 10 min; (D) after 60 min (all DSC curves without cooling below 600 K).

analogous data on the small 654 K endotherm. Figures 3 shows an example of the sintering at 610 K. It illustrates the continuous disappearance of the 618 K melting peak. The 654 K peak is at this temperature practically not at all affected. Much higher temperatures are needed to make its kinetics be observable, as is obvious from Table II. Figure 4 shows the fate of the 654 K melting peak on a much expanded heat capacity scale when the sintering is carried out at 650 K. At this high sintering temperature no crystalline polymer is left at the initial 618 K melting temperature, even at the shortest possible experiment (about 1 min).

Figure 5 is an example of partial reduction of the 618 K melting peak after sintering at 644 K for 5.5 min, followed by recrystallization of the molten

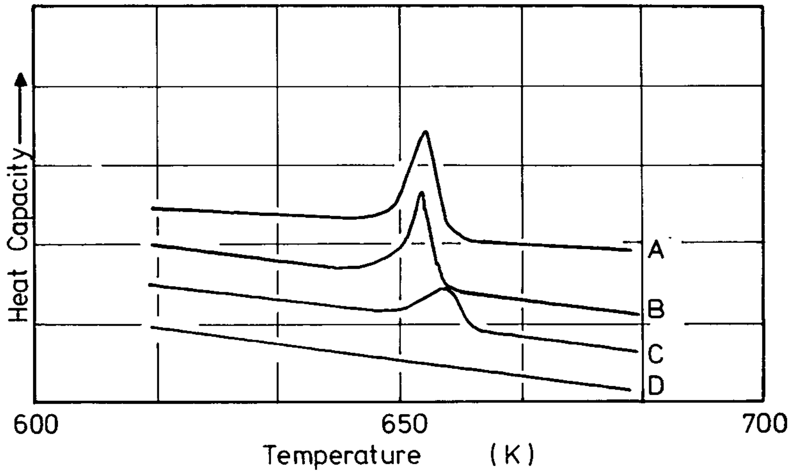

Fig. 4. DSC traces illustrating sintering of the extruded and drawn samples at 650 K: (A) 1 min; B) 60 min; (C) 120 min; (D) 720 min. (Note the higher sensitivity. All crystals showing a 618 K melting peak are molten under these conditions. See Table I.)

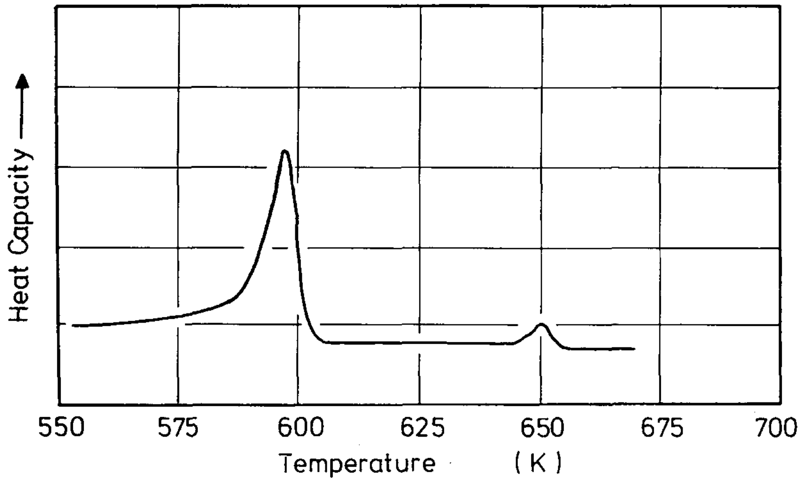

Fig. 5. DSC trace of an extruded and drawn sample sintered at 644 K for 5.5 min, followed by cooling to room temperature before analysis. (Note the melting peak at about 600 K, absence of the 618 K melting peak, and unchanged 654 K melting peak.)

PTFE. Under these conditions the 654 K peak is unaffected, no evidence of the 618 K peak is left, and all of the recrystallized PFTE melts at 600 K (heat of fusion of 1.61 kJ/mol, i.e., 40% crystallinity). Figure 6 illustrates, finally, the effect of subsequent annealing of a sample sintered first at 607 K 1080 min. The sample was cooled at 1 K/min to room temperature after the sintering and then annealed at 599 K for 50 h. This treatment increased the heat of fusion to 2.32 kJ/mol (57% crystallinity) and shifted the melting peak temperature up to 609.4 K.

Minor effects observed during long time sintering or annealing are small amounts of long-persisting 618 K melting PTFE (less than 1% crystallinity)

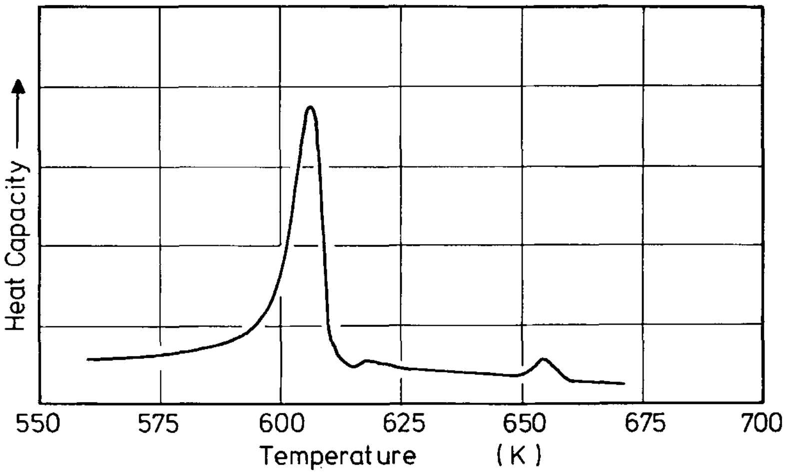

Fig. 6. DSC trace of an extruded and drawn sample sintered at 607 K for 1080 min, followed by cooling to room temperature and then annealing at 599 K for 50 h before analysis. (Note the change from Fig. 5. It involves improvement of the crystals melting before at 600 K, melting now at about 609 K. Note also the remaining small amount of crystals melting at 618 K.)

and a new small endotherm in the 630–650 K region. The latter falls in the region of the initial high temperature melting tail of the drawn material (step 2), without exceeding its overall heat effect.

DISCUSSION AND CONCLUSIONS

The materials after their respective mechanical and thermal treatments can be identified by their thermal behavior. The starting material has a 617–618 K peak temperature and a heat of fusion of 4.05 kJ/mol, i.e., it is close to 100% crystalline (Fig. 2, curve A). The extruded material is uniform, and little changed from the starting material, but develops a 1–2% heat of fusion in the 620–650 K temperature range (melting tail, Fig. 2, curve B). On long time sintering or annealing this melting tail may be the cause of minor endotherms due to rearrangements in the crystals (Fig. 6). The drawn, but unsintered material is not uniform along the sample. This accounts for some of the scatter observed in the experiments on sintering (Tables I and II). The drawn material shows a small, but significant decrease in heat of fusion (10–20%) and has a new endotherm at 654 K, 50 K above the equilibrium melting temperature (Fig. 2, curves C and D). This new endotherm corresponds to 1–3% crystallinity and may be due to strain in tie molecules between the remaining crystals causing superheating.[10] Sintering the crystals causes the 618 K melting peak to be removed first (Fig. 3). Next, one observes the reorganiza-

TABLE III
Time (min) to Reach the Indicated Crystallinity at the Given Temperature[a]

Crystallinity Sintering temp (K)	80%	60%	40%	20%	10%	5%
599	0.8	554.4	—	—	—	—
600	—	13.2	395.6	—	—	—
601	—	3.8	36.7	909.9	—	—
602	—	0.8	11.2	124.2	—	—
603	—	—	5.5	37.6	215.4	—
604	—	—	3.4	17.0	72.6	293.0
605	—	—	2.4	9.6	33.4	110.5
606	—	—	1.9	6.3	18.7	53.5
607	—	—	1.5	4.5	11.5	30.2
608	—	—	1.3	3.4	8.3	19.1
609	—	—	1.2	2.8	6.1	13.1
610	—	—	1.0	2.3	4.8	9.6
611	—	—	0.9	2.0	3.9	7.4
612	—	—	—	1.7	3.3	5.9
613	—	—	—	1.6	2.8	4.9
618	—	—	—	1.0	1.6	2.5
623	—	—	—	0.8	1.2	1.6
628	—	—	—	—	0.9	1.2
633	—	—	—	—	—	1.0
638	—	—	—	—	—	0.9
643	—	—	—	—	—	0.8

[a] Data are omitted when times decrease below 0.8 min or increase above 1000 min. These times are beyond the error limit of the equation, which is about 8% in crystallinity.

tion of the minor amount of the sample giving rise to the 620–650 K melting tail into more distinct endotherms of similar area (Fig. 6). The 654 K endotherm is, finally, affected only at the highest sintering temperatures (Fig. 4). On subsequent crystallization by cooling, a reduced crystallinity of about 40% is recovered which melts now at 600 K (Figs. 1 and 5). Annealing of this regrown crystallinity can increase the crystallinity to above 50% and shift the melting temperature to at least 610 K (Fig. 6).

These characterizations permit the description of the production sample illustrated in Figure 1. All the material melting at 599.7 K is recrystallized on cooling. None of the starting crystals are left. The crystals giving rise to the 610.3 K endotherm are not unmolten starting material, but are recrystallized material annealed during manufacture. The 654 K peak is indicating strain-caused superheating on a small amount of crystals produced in the drawing step.

The kinetic data of Table I allow also to establish likely limits on sintering conditions. All data of Table I can be fitted with an accuracy of about 8% in crystallinity to the following equation:

$$\log[-\ln(1 - \text{crystallinity})] = 0.241 - 0.043\Delta T(1 + 2 * \log t)$$

where ΔT is the difference in sintering temperature from 598 K, the assumed average melting temperature of PTFE. These data are also summarized in Table III.

This research, relying exclusively on thermal analysis, had led to a detailed characterization process for sintered PTFE products. It is possible to use these data for quality control as well as for process optimization. In addition, superheating of PTFE was reconfirmed, and the existence of thermally very highly resistant crystals was shown.

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