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DTA and DSC study on the effect of mechanical dispersion on poly(tetrafluorethylene) properties

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Abstract: Poly(tetrafluorethylene) particles were obtained by mechanical processing of the formed polymer (Teflon bar). In order to assess the effect of mechanical wear on polymer properties, their melting and crystallization behaviour was investigated by DSC and DTA, and the results were compared to the ones obtained for the native polymer. An increase of the crystallinity degree and an accentuated decrease of the average molecular weight were found for the samples submitted to mechanical wear, as a result of mechanical degradation of the polymer.

Keywords: Teflon, mechanical degradation, DTA, XRD, DSC.

Introduction

Industrial processing of poly(tetrafluorethylene) (PTFE) in order to obtain semi-products or finite products is similar to metal cutting and implies mechanical operations such as turning, milling, planning or

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drilling.¹ In all these operations, a considerable amount of polymer waste is obtained, and since the monomer preparation, polymer obtaining and formation are highly expensive the question arises about a potential re-use of the PTFE waste by thermal degradation for monomer recovery, a problem that was approached in a series of papers by Lucia Odochian and co-workers.^{2a-d}

As known, the stability of polymeric chains in respect to mechanical degradation decreases with increasing chain length, to the point that under a certain limit of the degree of polymerization the scission of the macromolecules becomes negligible, while it becomes relevant for high values of chain length.³

For commercial PTFE, the average molecular weight has very high values, of around 10^7 - 10^8 g/mol, and because of the structural peculiarities, the macromolecular chains are in a state of extended conformation.⁴ It is interesting to note that in an hypothetical case of a completely extended conformation, a PTFE macromolecule length would exceed 0.1 mm. Along with high PTFE chain rigidity, these considerations lead to the conclusion that the polymer has a low stability towards mechanical degradation, as suggested by previous studies on crystallinity and heat of fusion of PTFE wastes.⁵

In the present paper, crystallization and melting behaviour of formed PTFE (Teflon bar obtained by pressing and sinterization) and simulated PTFE wastes was investigated by DSC and DTA, in comparison to the native polymer. The study aims to evaluate the effect of mechanical processing on the polymeric material. For this purpose, the DSC analysis of the melting behaviour of the samples allowed us to investigate the changes in sample crystallinity, and the results were confirmed by XRD spectra.

DTA analysis of the crystallization process allowed us to evaluate the changes in the average molecular weight of the polymer as a result of macromolecular chain breaking under mechanical stresses.

Results and discussions

Four different PTFE samples were analyzed: native polymer, formed polymer and two samples of polymer particles, with particle diameters of 820 and 415 μm , respectively, obtained by turning.

DSC curves for the melting of the samples at a heating rate of 10 K/min are depicted in figure 1.

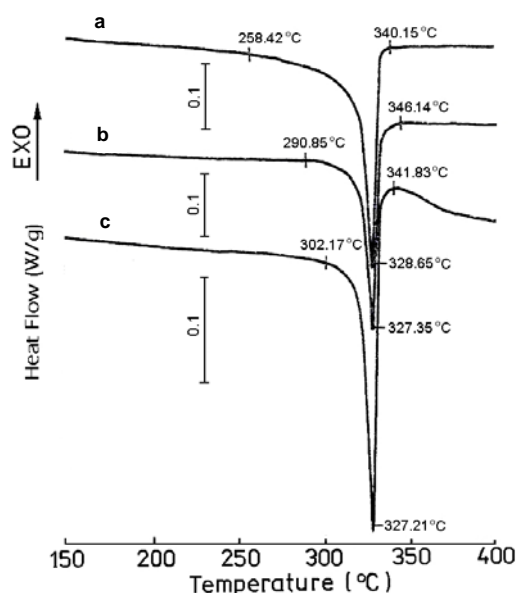


Figure 1. DSC spectra for formed PTFE (a), 820 μm (b) and 415 μm (c) PTFE particles.

Table 1 summarizes the characteristic temperatures (T_i – initial temperature of the melting peak, T_m – temperature at the maximum of the melting peak, T_f – final melting temperature, $\Delta T = T_f - T_i$ – melting temperature range,) and the melting enthalpy.

From the data in Figure 1 and Table 1 it is evident that the onset temperature of the melting peak increases significantly and the melting

temperature range decreases from formed PTFE to PTFE waste, while the melting enthalpy increases in the same order. This indicates an increase in crystallinity of the samples as an effect of mechanical stress, by rearrangement of the macromolecules when the material is under shear. These findings could also indicate an increase in chain mobility due to macromolecules' scission under mechanical stress, since an increase in PTFE crystallinity has been shown to correspond to a decrease in molecular weight of the polymer.⁶

Table 1. Characteristic temperatures and melting enthalpy from DSC spectra.

Sample	T _i (°C)	T _m (°C)	T _f (°C)	ΔT	ΔH _m (J/g)
Formed PTFE	258	329	340	82	25.8
PTFE 820 μm	291	327	346	55	28.4
PTFE 415 μm	302	327	342	40	28.9

These conclusions are also supported by XRD analysis, presented in figure 2. A qualitative analysis of the XRD spectra in figure 2 leads to the following conclusions:

- crystalline maxima overlaps with an amorphous background;
- some crystalline maxima appear in the same positions for all the samples (e.g. 8 °, 10 °, 18 °, 19 °, 32.5 °);
- the sample with the highest crystallinity degree is native PTFE, showing the most intense crystalline maxima;
- formed PTFE exhibits the lowest intensity of the crystalline maxima, while these intensities are higher for waste PTFE.

The crystalline maxima were separated from the amorphous background and the corresponding area was estimated for each component

by interpolation and numerical integration. The crystallinity degree was then estimated as the ratio of crystalline area to total area. Because of the inaccuracy in separating the two overlapping components in XRD spectra, the obtained values can be used only qualitatively, allowing a comparative discussion between samples. Nevertheless, the results confirm the conclusions drawn from the DSC results, the obtained crystallinity degree being: 82.3 % for native PTFE, 62.5 % for formed PTFE, 68.1 % for waste PTFE with 820 μm particle diameter, respectively 72.4 % for waste PTFE with 415 μm particle diameter.

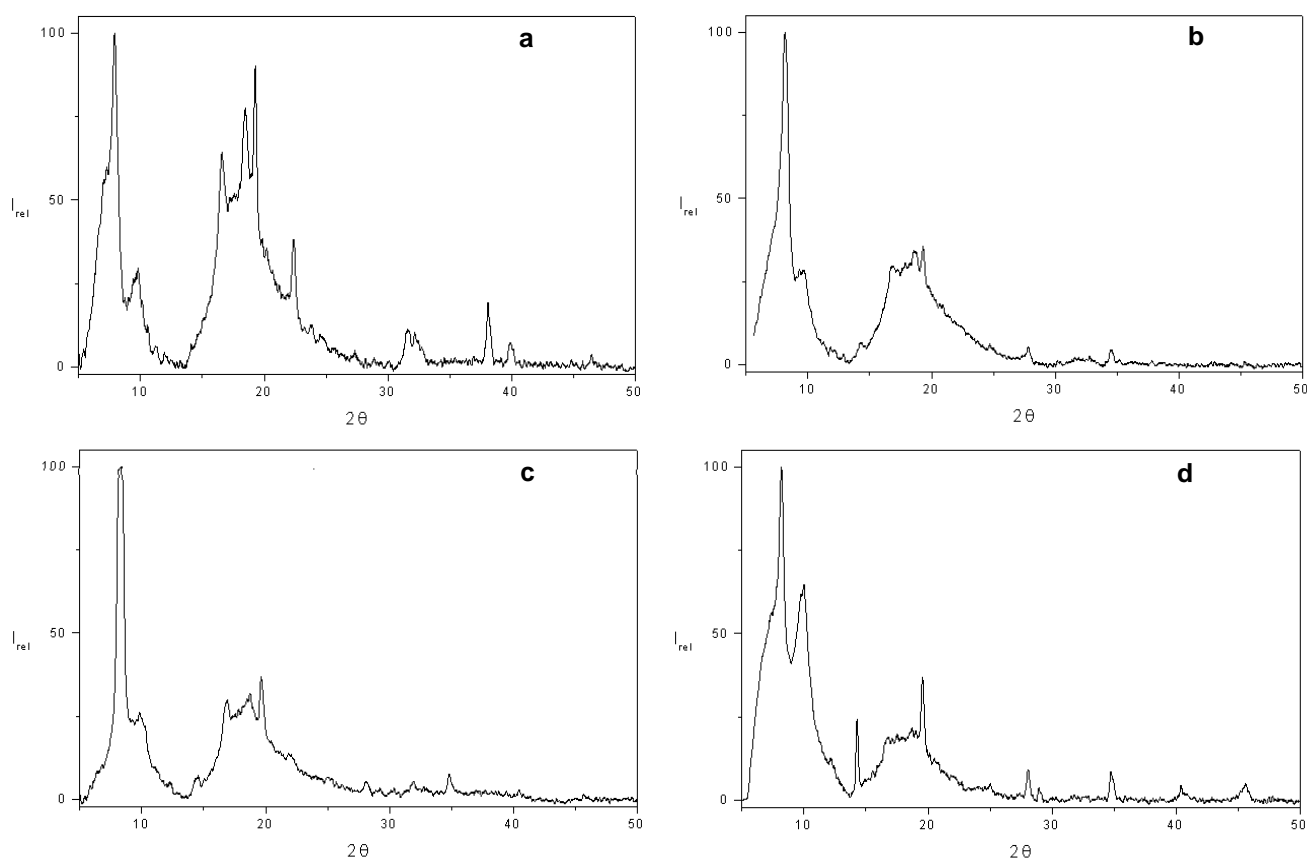


Figure 2. XRD spectra for native PTFE (a), formed PTFE (b), 820 μm (c) and 415 μm (d) PTFE particles.

For the DTA study of the polymer crystallization, the four samples were heated up to 400 $^{\circ}\text{C}$ with a heating rate of 15 K/min, kept there for 30 minutes and then cooled down to room temperature with different cooling

rates between 1 and 20 K/min. The crystallization enthalpy was then computed by interpolation of the DTA peak and numerical integration.

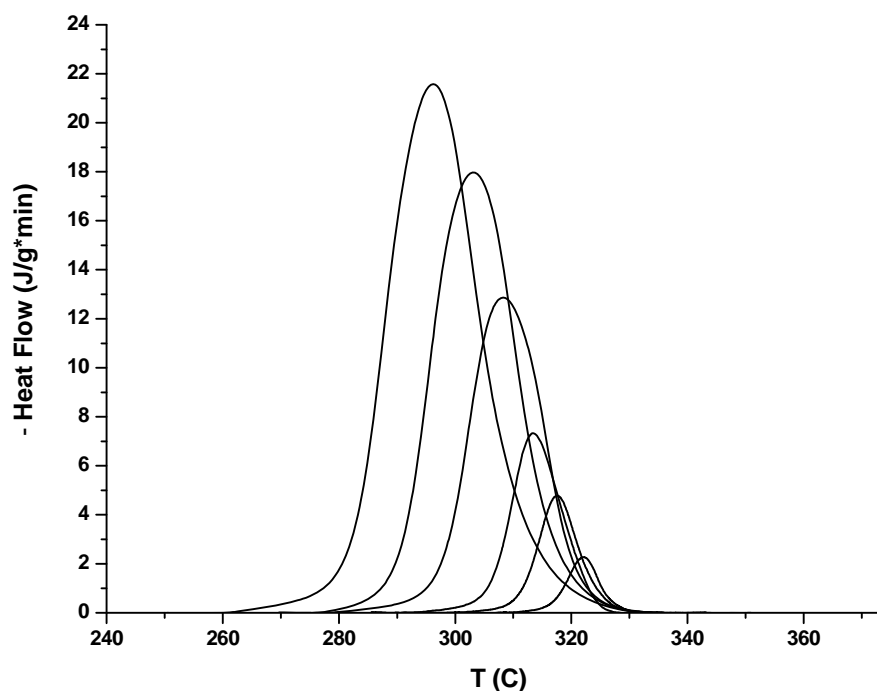


Figure 3. DTA peaks for the crystallization of native PTFE with different cooling rates: 1, 2, 4, 10, 15 and 20 K/min (from lowest to highest peak).

Table 2. Characteristic temperatures and crystallization enthalpy for native PTFE.

Cooling rate (K/min)	T_i ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH_{cr} (J/g)
1	330	322	311	-17.6
2	330	317	304	-20.1
4	330	313	295	-19.1
10	328	308	282	-19
15	329	303	278	-19.8
20	329	296	262	-19.6

In figure 3, the exothermal processes recorded as DTA peaks for the crystallization of native PTFE at different cooling rates are depicted, while

in Table 2 the characteristic temperatures and the crystallization enthalpy are summarized.

Similarly, DTA experiments were carried out for all the samples. The results are presented in tables 3-5:

Table 3. Characteristic temperatures and crystallization enthalpy for formed PTFE.

Cooling rate (K/min)	T_i ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH_{cr} (J/g)
1	330	326	318	-20.0
5	330	323	309	-18.9
10	329	315	290	-22.3
15	329	310	283	-22.1
20	329	305	272	-21.3

Table 4. Characteristic temperatures and crystallization enthalpy for waste PTFE with 820 μm particle diameter.

Cooling rate (K/min)	T_i ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH_{cr} (J/g)
1	332	327	321	-9.3
5	332	321	299	-27.3
10	331	312	290	-27.6
15	331	310	285	-28.1
20	331	307	260	-27.7

Table 5. Characteristic temperatures and crystallization enthalpy for waste PTFE with 415 μm particle diameter.

Cooling rate (K/min)	T_i ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH_{cr} (J/g)
1	333	325	317	-10.1
5	332	323	309	-27.6
10	332	315	291	-28.1
15	332	310	289	-29.1
20	332	307	259	-28.9

As it can be seen from the results in Tables 3-5, the characteristic temperatures are very similar for the crystallization of the four samples. The initial temperature of the crystallization is virtually independent on the cooling rate, while the maximum and the final peak temperatures are shifted to lower values with increasing cooling rate, as expected. The values of the crystallization enthalpy can be obtained by averaging the results, except for low cooling rates, where the small value of the heat flow leads to erroneous results. The values are presented in Table 6.

Table 6. Initial crystallization temperature and crystallization enthalpy for the PTFE samples.

Sample	T_i (°C)	ΔH_{cr} (J/g)	M_n (g/mol)
Native PTFE	329	-19.5	4.22 10 ⁶
Formed PTFE	329	-20.9	2.97 10 ⁶
PTFE 820 μm	331	-27.7	6.94 10 ⁵
PTFE 415 μm	332	-28.4	6.1 10 ⁵

As it can be seen, the absolute value of the crystallization enthalpy increases in the order: native PTFE (-19.5 J/g), formed PTFE (-20.9 J/g), PTFE 820 (-27.7 J/g), PTFE 415 (-28.4 J/g). This is consistent with the previous findings and can only be attributed to the fact that the average molecular weight of the polymer strongly decreases under mechanical stress, as a result of the breakage of the macromolecules.

Because PTFE is insoluble in the majority of solvents, the measurement of the average molecular weight cannot be performed by the methods commonly used for other polymers. For PTFE, this is usually done by rheological measurements with the molten polymer, method that lacks accuracy and can only be used in a restricted range of molecular masses.⁷ An alternative method relies on an empirical relationship between the

number average molecular weight M_n and the crystallization enthalpy (ΔH_C):⁸

$$\overline{M}_n = 2.1 \times 10^{10} |\Delta H_C|^{-5.16}$$

where ΔH_C is in cal/g while M_n in g/mol. The results are depicted in table 6. A slight decrease in the average molecular mass is observed for formed PTFE as compared to native PTFE, as a result of polymer degradation during forming. The decrease is much higher for the two samples of waste PTFE as compared to the formed polymer, from which waste PTFE was obtained, showing that mechanical wear leads to a mechanical degradation of the polymer, involving chain breaking, to such a degree that the average molecular weight drops drastically, with almost one order of magnitude.

Experimental

Native PTFE was supplied by Hoechst, Germany as granular polymer (under the commercial name Hostaflon TF 1645), with an average molecular mass of 10^6 g/mol.

The formed PTFE (bar of 40 mm diameter) was obtained from the granular polymer by pressing and sintering at the Chemical Factory of Victoria, Romania.

To simulate waste PTFE, polymer particles were obtained by turning from the PTFE bar with a stainless steel turning chisel. The obtained particles were screened and 6 fractions separated. Two of them, with average diameters of 820 μm and 415 μm , respectively, were then submitted to analyses.

DSC analyses were performed on a DSC-2950 Du Pont Canada apparatus, in N_2 stream, flow rate of 30 mL/min, heating rate of 10 K/min, sample mass ≈ 17 mg, temperature range of 25 – 450 $^\circ\text{C}$.

XRD analyses were carried out on a DRON-2.0 with data acquisition, under the following conditions: MoK α filtered radiation, $\lambda = 0.7107 \text{ \AA}$, 2θ recording.

DTA analyses were carried out on a Diamond Pyris TG-DTA thermobalance (Perkin-Elmer) under nitrogen flow. Temperature and heat flow calibration were done with Perkin-Elmer calibration reference materials.

Conclusions

Under the mechanical stress involved in the process of mechanical dispersion, the polymeric material undergoes shearing, especially in the amorphous regions, along with mechanical degradation that includes macromolecular chain breakage. As macromolecules' stability with respect to mechanical degradation decreases with increasing molecular weight, PTFE macromolecules with longer chains will be more susceptible to chain breakage, leading to a sharp decrease in average molecular weight.⁹ This conclusion is also supported by the increase of the crystallization enthalpy for the samples of waste PTFE as compared to the formed polymer.

As a result of the decrease in the average molecular weight, the molecular mobility in the amorphous regions increases and under the shear caused by the external mechanical force the macromolecules realign with the flow direction,¹⁰ with the direct result of an increase of the crystallinity degree, of the initial melting temperature and of the melting enthalpy of the polymer.

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