

STUDY ON THE INFLUENCE OF PTFE PARTICLE SIZE ON THE POLYMER THERMAL BEHAVIOR

I. Melting

*M. Dumitraş and L. Odochian**

Department of Physical Chemistry, 'Al. I. Cuza University', Iaşi, România

(Received December 22, 2001; in revised form May 2, 2002)

Abstract

The influence of the size of poly(tetrafluoroethylene) (PTFE) particles, obtained from the formed polymer (bar) by cutting on the fusion was studied in order to get information on the polymer breaking consequence.

Three fractions of particle diameters between 1.62–0.42 mm were submitted to DSC in nitrogen, DTA in air and DRX analyses and the results compared to those obtained with the non-processed formed polymer and PTFE mentioned in literature.

The study on the heating rate influence on the melting temperature range (ΔT) and the specific heat of fusion ($Q/J\text{ g}^{-1}$) carried out with the fraction of 0.82 mm diameter afforded a method for estimating the polymer specific caloric capacity by means of DSC data.

Keywords: DRX, DSC, DTA, formed PTFE, melting, waste PTFE

Introduction

Poly(tetrafluoroethylene) (PTFE) is a thermoplastic polymer with many technical applications due to its special properties [1a]. Since the monomer preparation, polymer obtaining and formation are highly expensive [1b] the question arises about a potential re-use of the PTFE waste [2a, 2b, 2c, 3, 4]. In this purpose, some aspects have been approached regarding the effect of polymer breaking on the thermal behavior of the waste resulting by obtaining of various PTFE pieces, the subject being rather less studied.

The formed polymer is subjected to cutting by turning, milling, planning or drilling. This processing procedure of PTFE semi-products is largely applied [1c].

In order to get more information in this field, in the present paper the influence of the PTFE particle size of 1.62–0.42 mm diameter, obtained from the formed (bar) polymer by cutting, on the melting was studied.

In this purpose, proper thermal methods [5–7, 8a], such as DSC in N_2 and DTA in air, have been applied. The obtained results were confirmed by the DRX spectra.

* Author for correspondence: E-mail: lodochian@yahoo.com

The characteristic thermal amounts of the fractions were compared to those of the non-processed formed polymer and to the PTFE literature data [9–11].

At constant heating rate and sample mass both the characteristic fusion temperatures and the heat of fusion are influenced by the PTFE particle size. The study on the influence of the heating rate at constant particle size and sample mass on the melting range (ΔT) and on the heat of fusion ($Q/J\text{ g}^{-1}$) afforded the development of a method for estimating the polymer specific heat ($c_p/J\text{ g}^{-1}\text{ K}^{-1}$).

Experimental

The PTFE bar of 40 mm diameter was obtained from the granular polymer (particle diameters within the 300–700 μ range) by pressing at the Chemical Factory of Victoria (Romania). Its main features are $M_n \cong 10^5$ and a crystallinity degree of 68%.

The waste obtained by cutting was screened and 15 fractions separated. Three of them were then submitted to analyses by DSC in N_2 , DTA in air and DRX. Their average diameters were of 1.62 mm (1620 μ) – sample 2, of 0.82 mm (820 μ) – sample 3 and 0.42 mm (420 μ) – sample 4, respectively.

The DSC and DTA analyses were run by means of the following apparatus:

I. DSC-2950 DuPont Canada apparatus, in N_2 stream, flow rate of 30 mL min^{-1} , heating rate of 2.5 and 10 $^\circ\text{C min}^{-1}$, sample mass of 17 mg, temperature range of 25–450 $^\circ\text{C}$;

II. Derivatograph, (MOM-Hungary) with simultaneous recording of T, TG, DTG and DTA curves under the following conditions: heating rate of 10 $^\circ\text{C min}^{-1}$, sample mass of 100 mg, temperature range 25–450 $^\circ\text{C}$, static ambient atmosphere and newly calcined Al_2O_3 as reference material.

The DRX analysis was carried out on a TUR M-62 apparatus under the following conditions: $U=3\text{ KV}$, $I=20\text{ mA}$, counter rate 1 $^\circ\text{ min}^{-1}$, 2θ recording, sample mass 0.3 mg.

Results and discussion

The DSC curves recorded in N_2 for the samples 1, 3 and 4 are depicted in Figure 1 and the characteristic thermal quantities of the fusion listed in Table 1.

Table 1 Thermal amounts characteristic of melting of samples 1, 3 and 4 from DSC data at 10 $^\circ\text{C min}^{-1}$

N ^o	Sample	<i>m</i> /mg	<i>a</i> / $^\circ\text{C min}^{-1}$	<i>T</i> _i / $^\circ\text{C}$	<i>T</i> _{max} / $^\circ\text{C}$	<i>T</i> _f / $^\circ\text{C}$	ΔT / $^\circ\text{C}$	<i>Q</i> / J g^{-1}
1.	PTFE bar	17.1	10	258.42	328.65	340.15	81.73	25.84
3.	<i>d</i> ₂ =0.82 mm	15.8	10	290.85	327.35	346.14	55.29	18.41
4.	<i>d</i> ₃ =0.415 mm	11.8	10	302.17	327.21	341.83	39.66	14.35

where *T*_i – temperature of fusion beginning, *T*_m – temperature at the maximum of the melting peak ('melting temperature' [9]), *T*_f – final melting temperature, $\Delta T = T_f - T_i$ – melting temperature range, *Q* (J g^{-1}) – specific heat of fusion.

T_i was found to increase with decreasing particle size which would indicate an increased crystallinity, as confirmed by the DRX spectra.

The DRX spectra of the samples 1, 2 and 3 in Fig. 2a, b and c show an intensification of the diffraction lines in the crystalline regions as the PTFE particle size decreases.

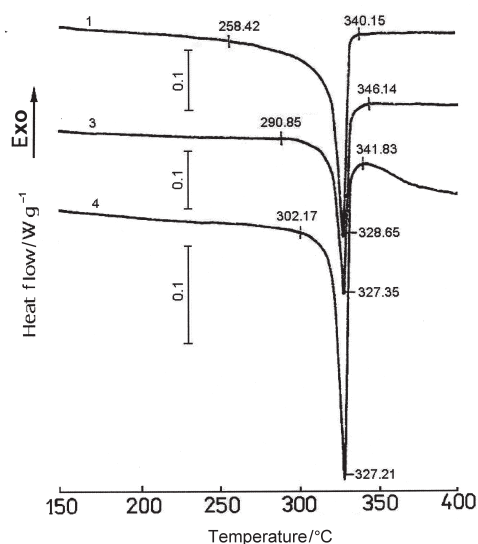


Fig. 1 DSC melting curves of samples 1, 3 and 4 at a heating rate of $10^{\circ}\text{C min}^{-1}$

The melting temperature (T_m) shows a slight decreasing tendency, which would suggest the polymer average molecular mass to decrease with decreasing particle size. This finding is correlated with the above mentioned effect, of crystallinity increase in the same order by taking the fact into account that the mechano-dispersion proceeds firstly by destroying the regions of low crystallinity where the molecular mass is higher, as mentioned in literature [12a].

The specific heat of fusion ($Q/\text{J g}^{-1}$) decreases significantly with decreasing PTFE particle size. This finding could be explained by the difference between the low-molecular compounds where $Q=\lambda$ (specific latent heat of fusion) and the macromolecular compounds showing a melting range [8b] where the sample requires a heat amount to heat up from T_i to T_p , this amount being expressed by the term $\bar{c}_p \Delta T$ (where \bar{c}_p is the average specific heat capacity of the biphasic solid-liquid system over the ΔT range). Since the interface area increases significantly with decreasing particle size the energy balance must be performed by also taking into account the contribution of the system's superficial energy by means of a term of the $S\sigma$ form, where S is the specific area and σ is the superficial tension, defined, after Harkins, as half the amount of energy necessary for breaking the intermolecular bonds that pass through a unitary area [12b, 13].

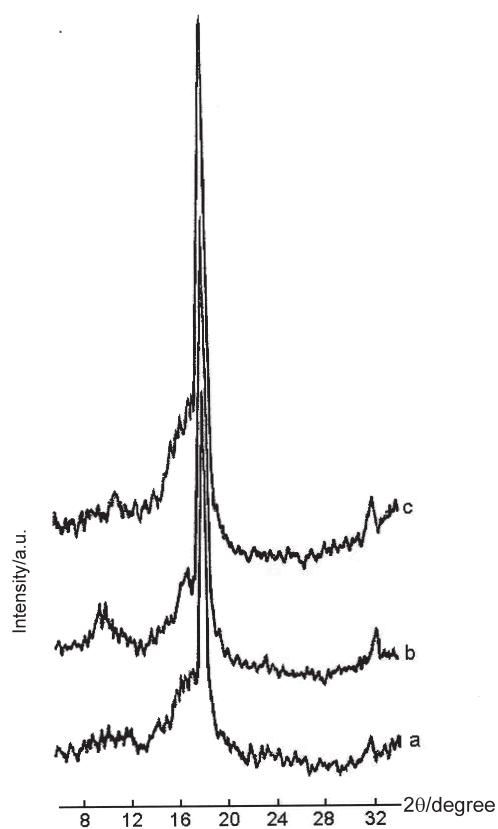


Fig. 2 DRX spectra of samples 1 (2a), 2 (2b) and 3 (2c)

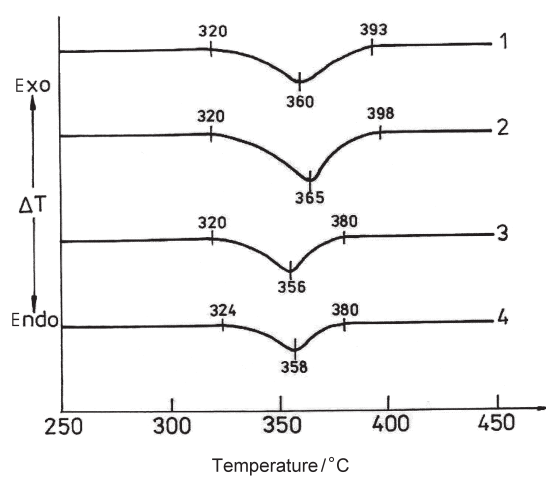


Fig. 3 DTA melting curves of samples 1, 2, 3 and 4 at a heating rate of $10^{\circ}\text{C min}^{-1}$

It follows that the specific heat of fusion (Q) for the fractions under study is given by the relationship:

$$Q = \bar{c}_p \Delta T + \lambda - S\sigma \quad (1)$$

which would explain the specific heat of fusion decrease with decreasing particle size.

The melting range, ΔT , decreases with decreasing PTFE particle size as a consequence of temperature gradients diminution.

The characteristic melting thermal amounts of the samples 1, 2, 3 and 4 resulting from the DTA curves recorded in air (Fig. 3) are presented in Table 2.

Table 2 Thermal amounts characteristic of melting of samples 1, 2, 3 and 4 from DTA data at $10^\circ\text{C min}^{-1}$

N°	Sample	m/mg	a/ $^\circ\text{C min}^{-1}$	$T_i/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_f/^\circ\text{C}$	ΔT	$A_{\text{DTA}}/\text{mm}^2$
1.	PTFE bar	99.97	10	320	360	393	73	23
2.	$d_1=1.26$ mm	100.01	10	320	365	398	78	21.5
3.	$d_2=0.82$ mm	100.05	10	320	356	380	60	19.25
4.	$d_3=0.415$ mm	100.03	10	324	358	380	56	14.5

These amounts show the same evolution as also shown by the DSC curves. The temperature interval, ΔT , and the DTA peak area, which represents a measure of the thermal effect of the fusion, also decrease with decreasing particle size supporting thus the DSC results. While the ΔT amounts from DTA and DSC data are comparable, the T_i , T_m and T_f temperatures resulting from DTA are higher, being mainly influ-

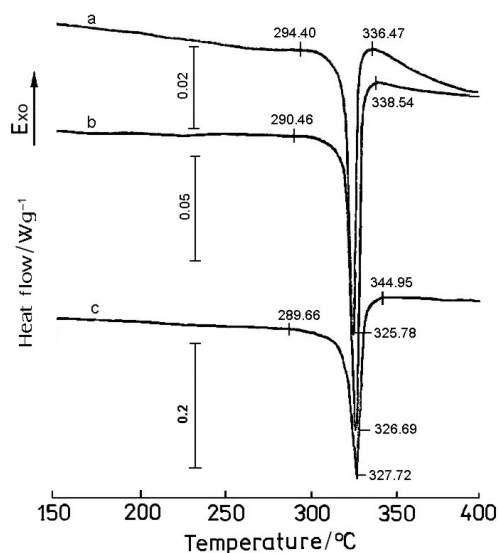


Fig. 4 DSC melting curves of sample 3 at heating rates of 2 (4a), 5 (4b) and $10^\circ\text{C min}^{-1}$ (4c)

enced by the sample mass under study (100 mg in DTA and 16 mg in DSC), the DSC melting temperatures, T_m , being close to literature ones (332°C) [10, 14].

In Fig. 4, the DSC curves for the sample 3 are drawn for various heating rates, of 2, 5 and 10°C min⁻¹, and invariable sample mass (16 mg). The characteristic thermal amounts are presented in Table 3.

The analysis of the above data afforded the study on the influence of temperature gradients which varied due to the various heating rates on the thermal amounts ΔT and Q . The increase in the temperature gradients with increasing heating rate results in the enlargement of the melting temperature interval.

Table 3 Thermal amounts characteristic of melting of sample 3 from DSC data at various heating rates

N°	Sample	m/mg	$a/^\circ\text{C min}^{-1}$	$T_i/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_f/^\circ\text{C}$	ΔT	$Q/\text{J g}^{-1}$
1.	0.82 mm	15.37	2	294.4	325.78	336.47	42.07	12.39
2.	0.82 mm	17.42	5	290.46	326.69	338.54	48.08	15.63
3.	0.82 mm	16.65	10	289.72	327.72	344.95	55.29	17.15

The dependence $\Delta T=f(a)$, where a stands for the heating rate, obtained by assigning the experimental data (Table 3) described by the equation:

$$\Delta T = -0.0702a^2 + 2.4954a + 37.362 \text{ (}^\circ\text{C)} \quad (2)$$

afforded the extrapolation of ΔT at $a=0^\circ\text{C min}^{-1}$ (quasi-stationary analysis).

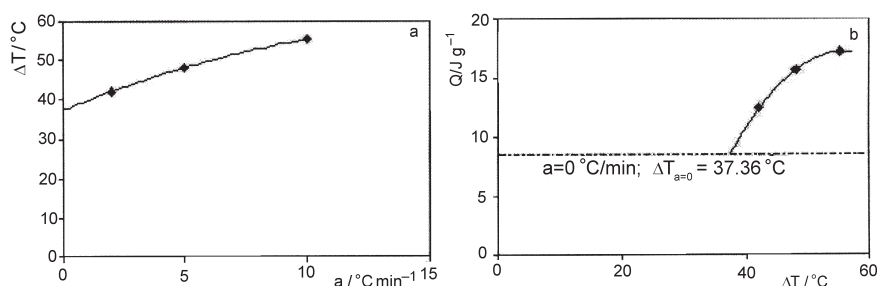


Fig. 5 ΔT vs. heating rate $^\circ\text{C min}^{-1}$ a (5a) and Q vs. ΔT (5b) for sample 3

A similar judgment based on the $Q-\Delta T$ dependence experimentally found (Table 3) and given by the equation:

$$Q = -0.0248(\Delta T)^2 + 2.7777\Delta T - 60.519 \text{ (J g}^{-1}\text{)} \quad (3)$$

led to the Q value for the quasi-stationary conditions, Q_c , as the temperature gradients disappear with heating rate becoming equal to zero. The ΔT_c and Q_c values for $a=0$ were obtained by the extrapolation of the curves $\Delta T=f(a)$ and $Q=f(\Delta T)$ in Figs 5a and b:

$$\Delta T_c = 37.36^\circ\text{C}, Q_c = 8.641 \text{ (J g}^{-1}\text{)} \quad (4)$$

According to Eq. (1) for the sample 3, where λ and $S\sigma$ are constant for the same sample, the average specific heat capacity \bar{c}_p is given by the equations:

$$\bar{c}_p(\Delta T) = \left(\frac{\partial Q_{\text{exp}}(\Delta T)}{\partial(\Delta T)} \right)_{\lambda, S} \quad (5)$$

$$\bar{c}_p(\Delta T) = -0.0496\Delta T + 2.7777 \text{ (J g}^{-1}\text{K}^{-1}\text{)} \quad (6)$$

The resulting value of $\bar{c}_p = 0.9260 \text{ J g}^{-1}\text{K}^{-1}$ is in good agreement with experimental ($0.96 \text{ J g}^{-1}\text{K}^{-1}$) [10] and theoretical ($0.98 \text{ J g}^{-1}\text{K}^{-1}$) [11] literature data, for both solid and molten PTFE, which confirms the validity of the advanced method.

The amounts ΔT_c , Q_c and afforded the estimation of the contribution of the $S\sigma$ term to the experimental value of the specific heat of fusion (Eq. (1)), where $\lambda = \Delta H_m = 0.82 \text{ J g}^{-1}$ [10]. The obtained value of 26.719 J g^{-1} indicates the particle size to influence significantly the characteristic thermal amounts of fusion.

Conclusions

The study on the influence of PTFE particle size on the melting process afforded the following conclusions to be drawn:

- The thermal melting characteristic amounts are influenced by the particle size and their evolution resulting from DSC and DTA data are similar;
- The average molecular mass was found to decrease with decreasing particle size while the crystallinity increased in the same order, as supported by DRX spectra;
- The enlargement of the temperature gradients with increasing particle size and with increasing heating rate results in the enlargement of the melting temperature interval as well as in the increasing of the heat of fusion;
- The increase in the interface area with decreasing particle size brings a significant contribution to the experimental value of the heat of fusion;
- The analysis of the heating rate influence on the characteristic thermal amounts ΔT and Q afforded a new method advanced for estimating the specific caloric capacity of PTFE from DSC data.

References

- 1 I. Lupușiu and N. Dușu, 'Poli(tetrafluoretilena) și folosirea ei în industrie', Editura tehnică, București (1977), a) p. 35; b) p. 73; c) p. 65.
- 2 S. Gaur and Th. B. Reed, 'Thermal Data for Natural and Synthetic Fuels', Marcel Dekker Inc., New York–Basel–Hong Kong 1998, a) p. 185; b) p. 187; c) p. 197.
- 3 N. Kiran, E. Ekincib and C. E. Snapec, Resources, Conservation and Recycling, 29 (2000) 273.
- 4 C. M. Simona and W. Kaminska, Polym. Degr. and Stability, 62 (1998) 1.
- 5 H. Yoshibo, R. Kinoshita and Y. Teramoto, Thermochim. Acta, 264 (1995) 173.

- 6 J. Schmidtke, G. Strobl and T. Thum-Albrecht, *Macromolecules*, 30 (1997) 5804.
- 7 Shibusachi, H. Saitoh and K. Chiba, *J. Thermal Anal.*, 49 (1997) 115.
- 8 N. Hurduc, 'Metode de caracterizare a polimerilor, I Calorimetria diferențială', Ed. Univ. Tehnică, Gh. Asachi' Iași, 1996, a) p. 26; b) p. 99.
- 9 D. W. Van Krevelen, 'Properties of Polymers, Third completely revised Edition', Elsevier Amsterdam, Lausanne, New York, Oxford, Singapore, Shannon, Tokyo 1997, p. 109.
- 10 B. Wunderlich, S. Z. D. Cheng and K. Lanfakis, 'Thermodynamic Properties of Polymers', *Encyclopedia of Polymer Science and Engineering* Vol. 16, Wiley New York 1989, p. 767.
- 11 H. W. Starkweather, P. Zoller and G. A. Jones, *Polym. Phys.*, 27 (1989) 993.
- 12 Cl. Vasiliu Oprea, Alex. Constantinescu and P. Bârsănescu, 'Ruperea polimerilor', Editura Tehnică, București, 1991, a) p. 133; b) p. 140.
- 13 E. Chifu, 'Chimia coloizilor și a interfețelor', Presa Universitară Clujeană, Cluj-Napoca, 2000, p. 69.
- 14 M. F. Fleszar, *J. Thermal Anal.*, 49 (1997) 219.