

MECHANICAL AND PHYSICAL CHARACTERISATIONS OF POLYTETRAFLUOROETHYLENE BY HIGH VELOCITY COMPACTION

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ABSTRACT: Commercially available PTFE is a thermoplastic polymer of unusually high molecular weight. PTFE cannot be manufactured with the conventional techniques used for lower molecular weight polymers such as extrusion or injection molding, and its current processing is long and expensive. A new process, High Velocity Compaction (HVC), allows processing PTFE within short processing times. In HVC, repeated impacts at a temperature close to but below the polymer melting point leads to a good sintering of semi-crystalline polymer powders. Physical and mechanical properties of PTFE processed by HVC are investigated showing that density, crystal weight fraction and wear properties are improved compared to the conventional sintering technique.

KEYWORDS: PTFE, processing, sintering, physical properties

1 INTRODUCTION

Polytetrafluoroethylene (PTFE) is a well-known and commonly used polymer material in various applications involving exposures to high temperatures and/or highly corrosive environments. However, certain mechanical properties of PTFE (such as weak creep resistance) limit its use.

Processing PTFE is problematic due to its high molecular weight. It induces a very high melt viscosity that prevents PTFE from being processed by conventional melt processes (extrusion and injection molding). Therefore, processes inspired by powder metallurgy such as cold compaction followed by sintering [1], compression molding, or hot isostatic pressing have been developed. They also include direct forming of shaped articles by cold compaction of PTFE powder, followed by “free sintering” at temperatures above the melting point of the virgin polymer. Those processes offer satisfactory solutions to viscosity issues, but applications are limited because processing is long and expensive.

A new technique, High Velocity Compaction (HVC), allows processing of semicrystalline polymer powders via sintering. HVC has first been developed for ceramic and metallic powders forming, it consists in applying high velocity impacts at room temperature on a powder-filled die to form a green part that is sintered afterwards. At CETIM (Technical Center, France), the HVC press has been adapted for compaction at relatively elevated temperature. Combination of repeated impacts and elevated temperature makes polymer powder sintering

occurring during forming. This technique allows processing semi-crystalline polymers without viscosity limitation, and appears to be well suited for POM [2], PA and UHMWPE [3]. Indeed, it has been shown that good sintering of this semi-crystalline polymer powders is possible thanks to repeated impacts at a temperature close to but below the polymer melting point.

This paper presents:

- a) the process parameters chosen for manufacturing PTFE by HVC;
- b) the comparative physical and mechanical characterization of PTFE processes by HVC and by the Conventional Sintering (CS) technique.

2 MATERIAL AND PROCESS

2.1 PTFE POWDER

Two commercial PTFE powders have been used in this study: Teflon® 807-N (figure 1a) and Teflon® 701-N (figure 1b) produced by Dupont.

Teflon® 807-N is a free flowing PTFE granular resins designed for compression moulding and ram extrusion (low back pressure) with high apparent density (1000g/l) and large particle size (average diameter: 600µm).

Teflon® 701-N is a fine-cut high-property resin (average granular size: 20µm) of medium apparent density (430g/l).

Both powders are characterized by a high crystallinity degree (approximately 80%) and a high melting point

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(330°C) that are irreversibly lowered after melting/recrystallization. Teflon® 701-N and Teflon® 807-N powders are all based on the same polymer and have an average molecular weight of $10^6 - 10^8$ g/mol.

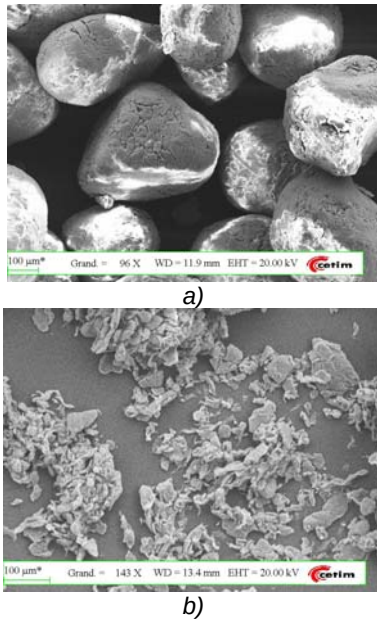


Figure 1: Scanning Electron Microscopy observations of PTFE powders. (a) Teflon® 807-N (b) Teflon® 701-N

2.2 HVC PROCESS AND PARAMETERS CHOICE

HVC consists in applying several controlled energy impacts on a powder-filled die. This fast and simple process allows high viscosity polymers forming and avoids shrinkage, as the process temperature is kept close to but below the polymer melting point.

High Velocity Compaction of polymer can be described in three main steps (figure 2): powder filling (A), compaction (B) and ejection (C). First of all, the die is filled (A) with 50g of polymer powder first heated in a stove for 30 minutes at the process temperature. Then, the upper punch is positioned into the die, and a 60MPa static pre-compaction is applied during 30s. Then, the press's hammer impacts the upper punch several times (B), leading to powder compaction. The following parameters are controlled: energy, frequency and number of impacts. Finally, before sample ejection (C), a 60 MPa static post-compaction is applied during 30s.

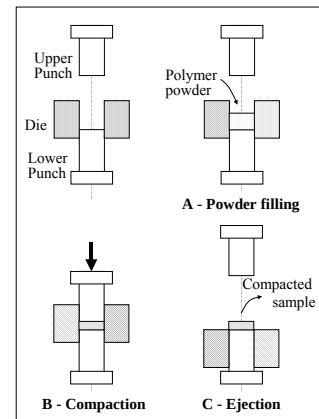


Figure 2: Main steps of HVC compaction.

The manufactured sample is a pebble with a 50mm diameter and a 10mm thickness (figure 3).



Figure 3: Sample produced by HVC

As a preliminary study, several process conditions have been tested:

- 70, 100 and 130 impacts,
- 700J, 1000J and 1600J per impact,
- 270°C, 305°C, 315°C, 325°C and 335°C for processing temperatures,
- 0.7, 1 and 3 impacts per second.

Samples obtained with (a) Teflon® 807-N (b) and Teflon® 701-N powders have also been compared.

The optimization of the HVC process parameters for PTFE has been done following:

- The appearance quality of the samples (presence of unevenness of the surface),
- The density and the density heterogeneity (observed thanks to X-ray photography),
- The mechanical properties revealed by tensile tests.

It was shown that the best materials properties are generally obtained with:

- 100 impacts
- 3 impacts per second
- an energy of 1000J per impact
- a processing temperature around 335°C,
- the powder Teflon® 807-N (instead of Teflon® 701-N powder).

Those parameters have been chosen to make a set of samples for comparative characterisations described in the following part.

3 COMPARATIVE CHARACTERIZATIONS

Physical and mechanical properties of PTFE processed by HVC and Conventional Sintering technique (CS) are compared. HVC and CS Samples were respectively machined in pebbles and in a tube. The CS tube was made by extrusion and then sintering of standard PTFE Teflon® 7A powder produced by Dupont.

3.1 DENSITY AND POROSITY MEASUREMENTS

Density measurements have first been carried out with a METTLER AE200 scale equipment (with an accuracy of 0.1mg) in compliance with ISO standard 1183 (Method A with ethanol immersion liquid, five specimens tested for each kind of sample). Results show that HVC samples have a higher bulk density than the CS ones with respectively 2.24 g/cm³ and 2.16 g/cm³.

As density varies with cristallinity degree and porosity, a mercury porosimeter has then been used to measure the pore characteristics of these samples.

The theory of mercury porosimetry is based on the physical principle that a non-reactive, non-wetting liquid will not penetrate pores until sufficient pressure is applied to force its entrance. Mercury is a non-wetting liquid for almost all substances and consequently it has to be forced into the pores of these materials. Pore size and volume quantification is accomplished by submerging the sample under a confined quantity of mercury and then increasing the pressure of the mercury hydraulically. The detection of the free mercury diminution in the penetrometer stem is based on a capacitance system, and the amount thus displaced is equal to that filling the pores. Three specimens have been tested for each kind of sample.

Results (Table 1) show that HVC samples exhibit a lower porosity and a lower total pore area than CS samples. Moreover, the skeletal density is higher for HVC samples than for CS ones. Nevertheless, HVC samples exhibit an average pore radius larger than CS ones.

Table 1: Pore characteristics

	total pore area (m ² /g)	average pore radius (μm)	bulk density (g/cm ³)	apparent (skeletal) density (g/cm ³)	porosity (%)
HVC samples	7,3	0,13	2,21	2,41	8,6
CS samples	11,7	0,02	2,12	2,34	9,3

The cristallinity degree for both samples are analysed in the next part.

3.2 CRISTALLINITY DEGREE MEASUREMENTS

The tests consist in comparing the cristallinity degree of both kinds of samples by differential scanning calorimetry (DSC). Analyses were carried out with THERMAL ANALYSIS Q 100 equipment. A mass of 7±1mg was chosen for each sample with a temperature ramp of 10°C/min.

The classical method to determine the crystal weight fraction X_c was used. It consists in dividing sample melting enthalpy by crystal polymer enthalpy (given at equilibrium melting temperature).

These analyses highlight that samples processed by HVC exhibit a high cristallinity degree (around 70%) compared to CS samples (55%). At the opposite with HVC process, this conventional process involving a melting stage leads to a significantly lower cristallinity.

3.3 MECHANICAL TESTS

3.3.1 Tensile tests and three point bending tests

Mechanical properties were first investigated by uniaxial tensile tests and then three points bending tests. Tensile specimens had a square cross section of 1.5mm*5mm and a gage length of 10mm. Bending specimens were 3mm thick, 5mm wide and 30mm long. Distance between the two external contacts was 25mm, and the crosshead displacement was 1mm/min. For each test, five HVC samples and five CS samples were tested.

3.3.2 Results

The stress/strain curve obtained for tensile tests are plotted in figure 4. Young's modulus and material ultimate properties were measured for each test. Results are shown in table 2.

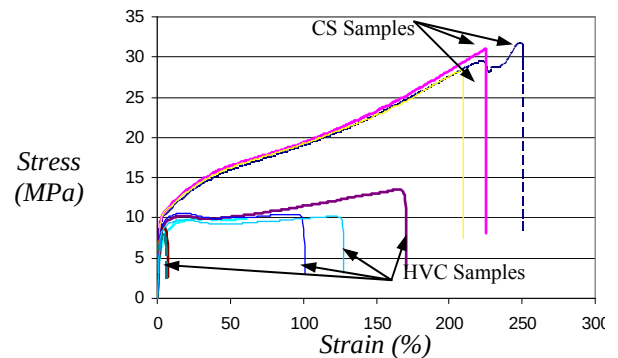


Figure 4: Stress/strain curves for tensile tests.

It can be seen that HVC samples exhibit a stiffness slightly higher (about 10%) than CS samples. Strength and fracture strain obtained by tensile tests are very weak for HVC samples compared to CS samples.

This gap in term of fracture properties between HVC and CS samples is also present for three points bending test but the difference observed is significantly smaller (table 2).

Moreover, standard deviations of HVC samples are high. It reveals a bad homogeneity of sintering quality.

Table 2: Mechanical tests results

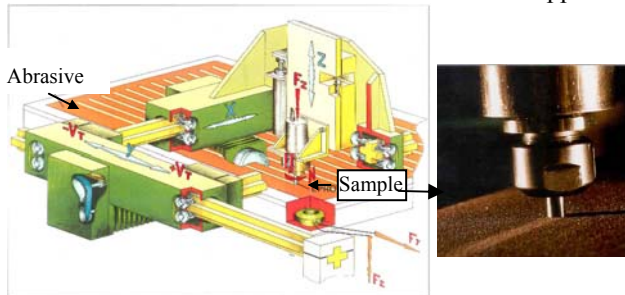
		Tensile tests			Three points bending tests		
		Young's Modulus (MPa)	Fracture strain (%)	Strength (MPa)	Young's Modulus (MPa)	Fracture strain (%)	Strength (MPa)
HVC Samples	Values	628	78,7	10,1	430	9,8	14,5
	Standard deviation	81	60,1	1,7	113	3,1	2
CS Samples	Values	563	222,4	29,6	393	13,5	17,5
	Standard deviation	20	27,3	1,8	36	0,2	0,5

3.3.3 Friction and wear measurements

Wear and coefficient of friction have been measured by two different tests: the Pin-Test and the PLINT Test. The principles and the conditions of each test are mentioned on the figures 5 and 6 and in tables 3 and 4.

• The abrasive Pin Test

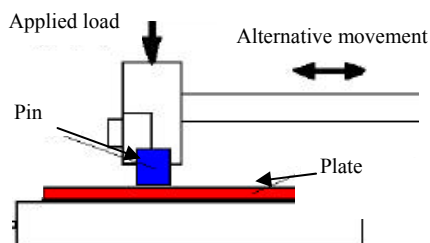
This test consists in putting a cylindrical specimen under load in rotation and translation onto an abrasive support.

**Figure 5: Principle of Pin Test****Table 1: Tests conditions**

Parameters	Values
Pin material	PTFE HVC and CS Samples
Abrasive; Load; Pressure	Al ₂ O ₃ ; 23 N; 0,72 MPa
Lubrication	dry
Rotation speed	20 rounds/min
Sliding speed	42,3mm/s
Length of track	533mm
Temperature	20°C

• The PLINT Test

The tests were carried out on an alternative PLINT TE-77 tribometer. This machine allows a relative movement between two objects in friction mode with different conditions.

**Figure 6: Principle of Plint Test****Table 4: Test conditions**

Parameters	Values
Pin material	PTFE HVC and CS Samples
Abrasive; Load; Pressure	XC38 Steel; 25 N; 2 MPa
Lubrication	dry
Frequency; stroke	5 Hz; 10mm533mm
Duration	16min40s
Temperature	20°C

• Results

Results obtained for both tests show that HVC samples have a wear resistance twice better than CS samples.

The coefficient of friction is similar for both processes specimens.

Table 5: Tribological tests results

		PIN TEST		PLINT TEST		
		wear rate (10 ⁻⁶ .mm.s ⁻¹)	μ _{moj}	weight wear (mg)	volumetric wear (mm ³)	μ _{moj}
HVC Samples	1	88,30	0,30	8,06	3,60	0,58
	2	55,20	0,29	8,37	3,69	0,55
	3	32,50	0,29	8,12	3,63	0,56
	Average	58,60	0,29	8,15	3,64	0,56
CS Samples	1	112,00	0,30	14,61	6,76	0,62
	2	96,40	0,31	14,71	6,81	0,61
	3	92,20	0,31	14,68	6,80	0,59
	Average	100,20	0,31	14,67	6,79	0,61

4 CONCLUSIONS

HVC process is attractive for PTFE for different reasons:

- The manufactory time to make a piece is very short compared to conventional process (two minutes against several hours);
- Density, crystal weight fraction and wear properties are improved.

Because of the high cristallinity, permeability and creep properties could also be improved. Ongoing tests will shortly give us the answer.

Lastly, higher temperature conditions (up to 360°C) will be tested to hopefully achieve better mechanical properties.

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