THE SPARK PLASMA SINTERING (SPS) AS A HIGH RAPID AND EFICIENT METHOD TO ELABORETE DENSE MATERIALS: APPLICATION FOR HIGH VISCOUS POLYMER

H. Lahlali[1], A. Mdarhri[1],* F. El Haouzi[1], I. El Aboudi[2], M. El Azhari[1], O. Lamé[3], D. Fabregue[3] and G. Bonnefont[3]

[1]*LMCN Laboratory, FSTG-Cadi Ayyad University, Marrakesh, Morocco*

[2]*LCME Laboratory, FSTG-Cadi Ayyad University, Marrakesh, Morocco*

[3]*Laboratoire MATEIS, INSA de Lyon, Villeurbanne, France*

*Corresponding author:a.mdarhri@uca.ma

Abstract:

This study demonstrates the efficiency of the spark plasma sintering (SPS) as a suitable technique to elaborate a dense polymer polytetrafluoroethylene (PTFE) which is difficult to sinter by conventional sintering methods e.g. hot pressing or hot iso-static pressing. Indeed, SPS is a very powerful technique not only to densify ceramics and dense metal, but also to prepare many kinds of material like alloys, polymers, composites. In this work we describe the experimental steps associated to the SPS process then the macroscopic and microscopic results such as the mechanical behavior, the thermal properties and the microstructural characteristics.

Résumé:

Cette étude montre l'efficacité du frittage flash (SPS) en tant que une technique convenable pour élaborer un polymère dense commelePolytétrafluoroéthylène (PTFE) qui est difficile à fritter par les techniques conventionnelles par exemple le pressage à chaud ou le pressage isostatique à chaud. En fait, SPS est une technique très puissante non seulement pour densifier la céramique et le métal dense, mais aussi de préparer de nombreux types de matériaux tels que des alliages, des polymères, des composites. Dans ce travail nous décrivons les étapes expérimentales associés au processus de SPS alors les résultats macroscopiques et microscopiques tels que le comportement mécanique, les propriétés thermiques et les caractéristiques de la microstructure.

Keywords: Conditions process, mechanical behavior, PTFE, spark plasma sintering.

1. INTRODUCTION

Polytetrafluroethylene (PTFE) is a high performance thermoplastic polymer with excellent features such as extreme thermal stability, low friction coefficients and dielectric constant[1]. The special properties of PTFE arise because of its strong chemical bonding (507 $kJ.mol^{-1}$), the shielding of its carbon backbone by fluorine atoms, and the intermolecular interactions between its very long, helical $(CF_2)_n$ chains. These special chemical and structural features also give extremely high melt viscosity (10^{11} P.s at 380°C)[2], and a negligible solubility in all common solvents. However, this high viscosity renders the manufacturing of the dense polymer by conventional sintering methods such as hot pressing, high temperature extrusion, and hot isostatic pressing more difficult, it needs extended holding times (hours) at higher temperatures [3].In this regard, spark plasma sintering (SPS),has been shown to be an effective unconventional sintering method for obtaining fully dense materials at lower sintering temperatures and shorter holding times (few minutes). The objective of this work is to briefly present the spark plasma sintering process as a suitable technique to elaborate a dense polymer polytetrafluoroethylene (PTFE). Secondly, the macroscopic and microscopic results such as the mechanical behavior, the thermal properties and the microstructural characteristics are discussed. We finish this experimental study by some remarks concerning the SPS process and underline the future work.

2. THE SPSPROCESS

Spark plasma sintering (SPS) is a newly developed rapid sintering technique which combines simultaneously the application of electric current and pressure directly on the sample (**Fig.1**).For conductive materials, the electrical current runs not only through the punch, made in a conductive material (usually graphite), and die but also through the particles. A spark can be induced between particles by the pulsed current. However, the densification mechanism for non-conductive (PTFE) materials during SPS is even less well understood. Munir and Shon suggested that the powders are heated by joule energy produced from the graphite die and punch[3] - [5].These particular sintering conditions allow sintering a broad range of materials very quickly and at lower temperatures than in conventional sintering.

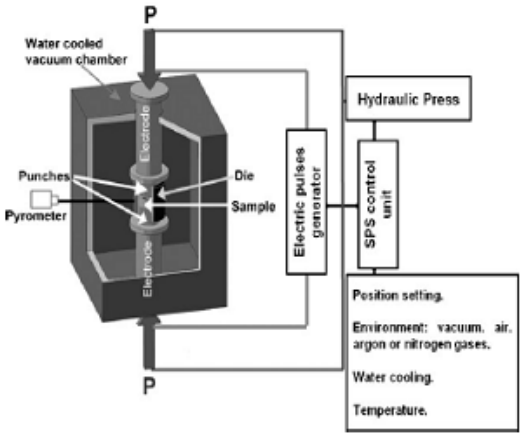

Fig. 1: Illustration of the SPS process.

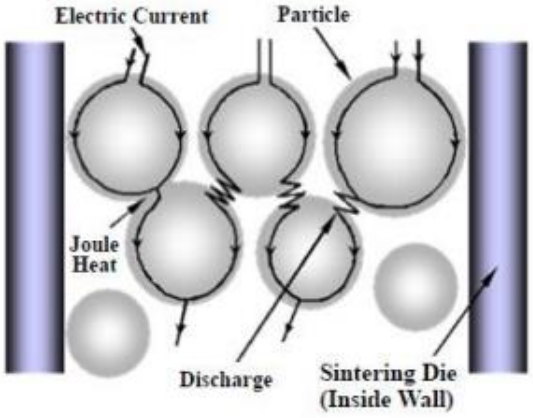

Fig. 2: Possible electric current path through powder particles inside the die.

This technique is original and quite recent. However, there is lack information on the exact mechanisms involved in this technique. For example, the existence of sparks or plasma in the powder to densify has not yet been proved. The electrical discharge between powder particles results in localized and momentary heating of the particles surfaces up to several thousand degree Celsius [5] – [7]. Since the micro-plasma discharges form uniformly throughout the sample volume the generated heat is also uniformly distributed (see **Fig.2**). The particles surfaces are purified and activated due to the high temperature causing vaporization of the impurities concentrated on the particle surface. The purified surface layers of the particles melt and fuse to each other forming “necks” between the particles.

3. EXPERIMENTAL PROCEDURES

3.1-Materials

The PTFE powder used in the present study was provided by the Hoechst-Germany company under the commercial denomination of Hostaflon, namely:Native (Hostaflon TF1620). Crystallinity was determined by using an infrared spectroscopy (VERTEX 70) giving an average value of 66.29%.The specific surface area was measured from the BET experiments indicating a value of 12.14 m^2/g.

3.2-SPS operation

The sintering of the PTFE powder was carried out in a vacuum using a SPS system (Model SPS-FCT HP D25/1). To sinter a circular disk with a diameter of 40 mm, we need 15g of powder. The processing conditions that enable us to fabricate our samples from the PTFE powder are as follows: The values of the applied current, the holding time and the pressure were fixed at 2 kA, 60 sec and 25 MPa respectively. A proportional-integral-derivative system is used to control temperature and pressure during the process. Then, our analysis is focused on the effect of the sintering temperature and heating rate on the physical and mechanical properties.

4. RESULTS AND DISCUSSION

4.1-Microstructural characteristics

The PTFE powder was examined by scanning electron microscope (SEM) (Model-JEOL JSM–5500). The SEM observations were carried out on the PTFE powder dispersed in the suitable surfactant (2-propanol) during five hours and then deposited on a slide after dried in open air. Roughly, the

size distribution of the spherical particles is found to be about w=6.21µm, evolved format statistical analysis on different areas of a set of SEM images (see **Fig.3**).

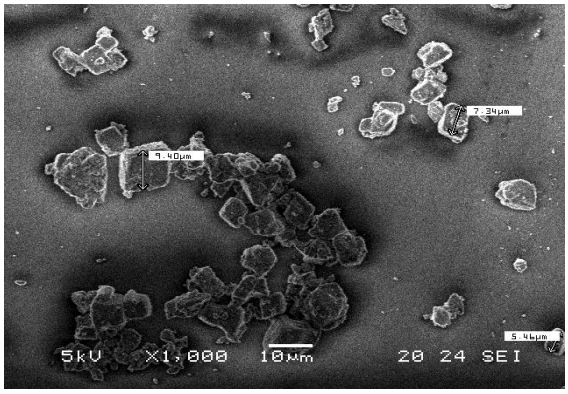

Fig. 3: Typical SEM micrograph indicating a micrometric particles size of the PTFE.

4.2-Thermogravimetric analysis

In thermogravimetric analysis (TGA) a sensitive balance is used to follow the weight change of the sample as function of temperature. In practice, this permits the assessment of thermal stability and degradation, among many others properties. From the results shown in **Fig.4**, the TGA curves of the PTFE samples, synthetized by the SPS process, show a very slight difference in all samples, also we find weight loss firstly became apparent between 400 ºC and 500 ºC and became rapid at ~ 550 ºC corresponding to 80% of weight loss.

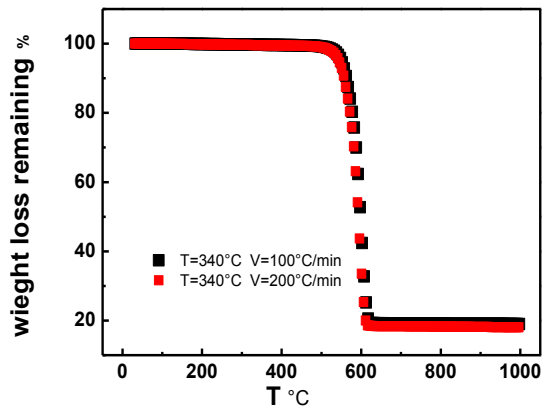

Fig. 4: Thermogravimetric curves of the PTFE samples synthetized by varying the process's parameters.

4.3-Mechanical behavior

An elegant way to assign the mechanical properties of synthetized PTFE materials to the changed of the polymer fabrication process is to perform three points bending test (Instron 3369 model). The dimensions of samples under test are 25mm×4mm×2mm. The experiments were carried out at room temperature. As mentioned above, the heating rate and the temperature are the only varied parameters. As a first step we have used the so-called Brazilian test as a rapid way to check the mechanical quality of so fabricated sample.

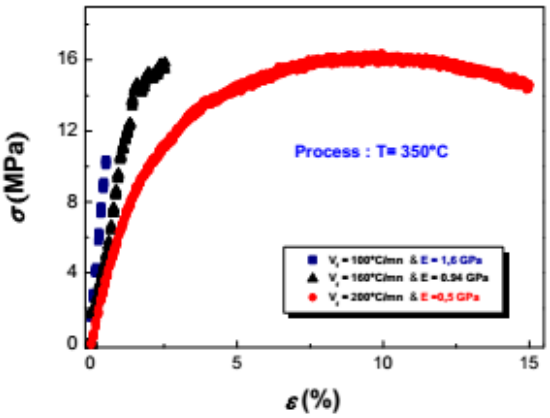

Fig. 5: stress/strain curves for T=350°C at differing heating rate.

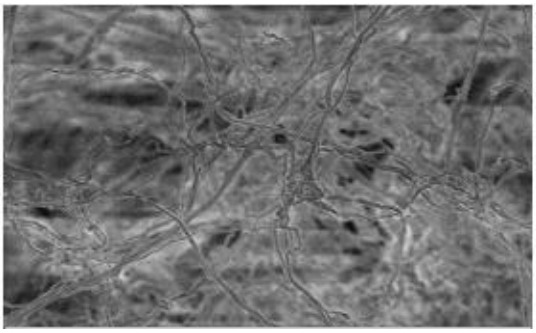

Fig. 6: Example of SEM micrographs of cryo-fractured surfaces of sintered PTFE.

Our data have demonstrated that the mechanical properties (elastic bending modulus, toughness, strength….) can be greatly tailored by adjusting the heating rate(**Fig.5**). Moreover, a similar effect is seen by varying the second parameter, i.e. sintering temperature (data not shown here) rendering the use of PTFE more advantageous in various applications. The examination of the microstructure of synthetized sample (curve in blue)(**Fig.6**) by using the SEM pictures shows the presence of several cavities that are responsible to the brittle state of the material. The observed micro-fibril structure is a characteristic of the high long chains of the polymer.

5. CONCLUSION

It is demonstrated that the mechanical properties of the PTFE can be varied widely according to the process parameters i.e. sintering temperature and heating rate. The best results have been obtained at brief time (1min). In addition, the measured thermal stability of these dense samples is extremely useful since their mechanical/electrical properties do not change for long time at temperatures as high as 250°C as it is expected. Efforts are now focusing on the development of 3D numerical models of the entire process in order to provide a predictive tool rendering the relationship between the process's parameters and the quality of the product more controllable. The future work will be focused on others properties associated to these experimental methods, e.g. dielectric properties.

ACKNOWLEDGEMENTS

This work is partially supported by INSA de Lyon (France). We are very grateful to our experimental collaborators Rachid (FSSM) and T. Charter (IUT Blois). We are also thankful to Professor M. Mansori for fruitful discussions.

REFERENCES

[1] A. Wall, Technology of Fluoropolymers, Second Edition, Wiley Interscience, New York, (1972).

[2] S. Borkar, B.Gu, M. Dirmyer, R. Delicado, A. Sen, Jackson, B. R. & Badding, J. V. Polytetrafluoroethylene nano/microfibers by jet blowing. Polymer (2006)47, p. 8337-8343.

[3] Z.A.Munir, U. Anselmi-Tamburini and M. Ohyanagi, The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. J Mater Science 41 (2006), p. 763–777

[4] M. Tokita, Mechanism of spark plasma sintering Mater Science. 83Forum. (1999), p. 308–311.

[5] I. J. Shon and Z. A. Munir, Synthesis Of mosi2-x Nb AND mosi2-y zro2 composites by the field-activated combustion method, Materials Science and Engineering A, A202, (1995), p. 256-261,

[6] K. Inoue, Method of making a heat exchanger U. S. Patent, No. 3,(1966), p.250,892.

[7] Xie GQ, Sintering process and interfaces microstructure of metal powders by pulse electric current sintering. Doctorat thesis. University ofNiigataJapan, (2003).