

Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Gabriel Guenoun

▶ **To cite this version:**

Gabriel Guenoun. Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles. Mécanique des matériaux [physics.class-ph]. Université Paris Saclay (COmUE), 2019. Français. ⟨NNT : 2019SACLN054⟩. ⟨tel-02504877⟩

HAL Id: tel-02504877

https://theses.hal.science/tel-02504877v1

Submitted on 11 Mar 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization



Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

université PARIS-SACLAY

NNT : 2019SACLN054

Thèse de doctorat

école normale supérieure paris–saclay

PTFE compact sintering: Physical mechanisms and models

Thèse de doctorat de l'Université Paris–Saclay
préparée à l'Ecole Normale Supérieure Paris–Saclay

École doctorale n°579 : Sciences Mécaniques et Energétiques, Matériaux et Géosciences (SMEMAG)
Spécialité de doctorat : Solides, Structures et Matériaux

Thèse présentée à Cachan, le 27 novembre 2019, par

M. Gabriel Guenoun

Composition du Jury :

M. Olivier Lame Professeur, Mateis, INSA de Lyon	Rapporteur
M. Yann Marco Maître de conférences (HDR), IRDL, ENSTA Bretagne	Rapporteur
Mme Sandra Domenek Maître de conférences (HDR), GENIAL, AgroParisTech	Examinateur
M. Lucien Laiarinandrasana Professeur, Centre des Matériaux, Mines ParisTech	Président du jury
M. Jean-Yvon Faou Ingénieur R & D, Saint-Gobain Research Paris	Invité
M. Stéphane Roux Directeur de Recherche CNRS, LMT, ENS Paris-Saclay	Invité
M. Gilles Régnier Professeur, PIMM, Arts et Métiers ParisTech	Co-directeur de thèse
M. Nicolas Schmitt Professeur, LMT, UPEC	Directeur de thèse

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

université PARIS-SACLAY
ÉCOLE DOCTORALE
Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

Titre : Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Mots clés : Science des polymères, Thermomécanique, Procédé, Modélisation, Cristallisation

Résumé : Le polytétrafluoroéthylène (PTFE) est un polymère semi-cristallin ayant de nombreuses propriétés remarquables avec notamment une excellente tenue thermique, un coefficient de frottement extrêmement faible et une grande résistance à la corrosion. Ces atouts lui valent d'être utilisé dans de nombreuses applications.

Sa mise en forme s'effectue par des procédés similaires à ceux utilisés pour les poudres métalliques. Dans l'un d'eux, la poudre de PTFE est compactée uniaxialement en pièces cylindriques. L'étape suivante est le frittage de la poudre compactée, au cours de laquelle les pièces sont chauffées au-delà de la température de fusion du polymère. Durant ce cycle thermique, les pièces subissent de grandes déformations causées notamment par la fusion et la recristallisation du PTFE. Les gradients thermiques couplés à ces déformations peuvent engendrer des incompatibilités mécaniques pouvant conduire à l'endommagement, voire à la rupture des pièces.

Cette thèse a permis d'apporter une compréhension plus fine des phénomènes physiques à l'œuvre durant le frittage du PTFE compacté par des observations et analyses microstructurales, et des essais de caractérisation thermique et mécanique. La relaxation de contraintes résiduelles, la fermeture de porosités et un phénomène de cristallisation secondaire ont ainsi été mis en évidence et génèrent des déformations libres de contraintes macroscopiques. Les propriétés mécaniques du matériau en température ont également été déterminées lors du frittage. Un modèle a été développé pour rendre compte de ces observations. Il a été intégré dans une simulation thermomécanique du procédé de frittage d'une pièce de référence. Le modèle a été validé par comparaison des résultats de la simulation à des mesures réalisées sur des expériences de laboratoire.

Enfin, un outil de simulation numérique par éléments finis a été développé. Il permet de déterminer les états de contrainte et déformation ainsi que la répartition des taux de cristallisation et des propriétés thermomécaniques au sein d'une pièce de PTFE compacté durant le cycle de frittage. A terme, cet outil pourrait permettre d'optimiser les paramètres du procédé industriel pour, par exemple, réduire le temps de frittage tout en s'assurant d'avoir des pièces non-endommagées et possédant les propriétés requises.

Université Paris–Saclay
Espace Technologique / Immeuble Discovery
Route de l'Orme aux Merisiers RD 128 / 91190 Saint-Aubin, France

AVA Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

université PARIS-SACLAY
ÉCOLE DOCTORALE
Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

Title: PTFE compacts sintering: Physical mechanisms and models

Keywords: Polymer science, Thermomechanics, Process, Modeling, Crystallization

Abstract: Polytetrafluoroethylene (PTFE) is a semi-crystalline polymer with many outstanding properties including excellent thermal resistance, extremely low friction coefficient and high corrosion resistance. These advantages make it suitable for many applications.

It is shaped by processes similar to those used for metal powders. In one of them, the PTFE powder is uniaxially compacted into cylindrical parts. The next step is the compacted powder sintering process, in which the parts are heated above the melting temperature of the polymer. During this thermal cycle, the parts undergo large strains caused by the melting and the recrystallization of PTFE. Thermal gradients coupled with these strains induce mechanical incompatibilities that can lead to damage or even failure of the parts.

This study provides a more detailed understanding of the physical mechanisms at work during the sintering of compacted PTFE through microstructural observations and analyses, and thermal and mechanical characterization tests. The relaxation of residual stresses, the closure of porosity and a secondary crystallization mechanism have thus been highlighted and generate macroscopic stress-free strain (called *eigenstrain*). The mechanical properties of the material as function of temperature have been also determined during sintering. A model has been developed to take into account these observations. It has been integrated into a thermomechanical simulation of the sintering process of a reference part. The model has been validated by comparing the simulation results with measurements from a laboratory experiments.

Finally, a finite element numerical simulation tool has been developed. It is used to determine the stresses and strains as well as the distribution of crystallization rates and thermomechanical properties within a PTFE part compacted during the sintering cycle. In the long term, this tool could make it possible to optimize the industrial process parameters to reduce sintering time, for example, while ensuring that the parts are undamaged and have the required properties.

Université Paris–Saclay
Espace Technologique / Immeuble Discovery
Route de l'Orme aux Merisiers RD 128 / 91190 Saint-Aubin, France

AVA Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Contents

Contents 7

Introduction 13
1 Polytetrafluoroethylene . . . 13
1.1 Discovery . . . 13
1.2 Properties . . . 14
1.3 Applications . . . 14
1.4 Synthesis . . . 15
2 Manufacturing process . . . 16
2.1 Overview of existing processes . . . 16
2.2 Challenges in the sintering of PTFE compacts . . . 17
3 Structure of the study . . . 18

1 PTFE sintering: state of the art 21
1 Microstructural evolution of PTFE during sintering . . . 22
1.1 Phase transitions . . . 22
1.2 Crystalline lamellae formation and growth . . . 24
1.3 Crystallization kinetics . . . 27
2 Mechanical analysis of PTFE sintering . . . 32
2.1 Mechanical behavior of PTFE during sintering . . . 32
2.2 Simulation of PTFE sintering . . . 36

2 Material and methods 41
1 Material . . . 43
1.1 PTFE resin . . . 43
1.2 Thermal characterization . . . 43
1.3 Sample preparation: cold pressing and slicing . . . 43
2 Differential scanning calorimetry (DSC) . . . 46
2.1 Method description . . . 46
2.2 Crystallinity evaluation from DSC† . . . 46
2.3 Thermal gradient effects . . . 47
3 Dilatometric measurements . . . 48
3.1 Method description . . . 48
3.2 Eigenstrain measurements† . . . 49
3.3 Crystallinity content evaluation from dilatometry . . . 50
4 X-Ray diffraction measurements (XRD)• . . . 51
4.1 Method description• . . . 51

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

4.2 Orientation measurement in transversely isotropic semi-crystalline polymers• . . . 53
4.3 Experimental setups• . . . 56
5 Microstructure observations . . . 58
5.1 Microtomography . . . 58
5.2 Scanning electron microscopy (SEM) . . . 58
6 Thermo-mechanical testings . . . 59
6.1 Dynamic mechanical thermal analysis (DMTA) . . . 59
6.2 Compression tests in thermal chamber . . . 60
6.3 Digital image correlation . . . 62
6.4 Infrared thermography . . . 63

I Thermal uniformity 65

3 Green PTFE behavior: residual stress relaxation 67
1 Introduction . . . 68
2 Behavior of nascent PTFE below melting* . . . 68
2.1 Reversible and irreversible eigenstrain decomposition* . . . 69
2.2 Proposed mechanisms for irreversible eigenstrains* . . . 73
2.3 Sintered PTFE* . . . 75
3 Behavior of nascent PTFE at melting . . . 76
4 Conclusions and perspectives* . . . 77

4 Void closure 79
1 Introduction . . . 80
2 Porosity estimation . . . 80
2.1 Compaction . . . 80
2.2 Scanning electron microscopy . . . 81
2.3 Microtomography . . . 83
2.4 Light diffusion analysis . . . 84
3 Void closure signature in dilatometry . . . 85
4 Conclusions and perspectives . . . 90

5 Behavior of PTFE from melt: crystallization and second melting 91
1 Introduction . . . 93
2 Crystallization of PTFE from melt . . . 93
2.1 Calorimetric measurements† . . . 93
2.2 Crystallization dependence with cooling rate† . . . 94
2.3 Crystallization kinetic model . . . 97
2.4 Equivalence between dilatometric and calorimetric measurements . . . 101
3 Anisotropic behavior . . . 102
3.1 Anisotropic thermal eigenstrain† . . . 102
3.2 Crystalline orientation measurement• . . . 105
3.3 Secondary crystallization as non linear heat capacity† . . . 107
4 Conclusions and perspectives . . . 108

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

6 Thermomechanical behavior of PTFE 111
1 Introduction . . . 112
2 Elasticity and viscoelasticity . . . 112
2.1 Dynamic mechanical thermal analysis (DMTA) measurements . . . 112
2.2 Compression tests inside thermal chamber . . . 114
3 Plasticity . . . 116
3.1 Plasticity evolution with crystallization . . . 117
3.2 Memory effect . . . 118
4 Thermomechanical model . . . 120
4.1 Green PTFE . . . 120
4.2 Sintered PTFE . . . 121
5 Conclusions and perspectives . . . 123

II Thermal inhomogeneity 125

7 Model equations: application to a semi-infinite PTFE part 127
1 Introduction . . . 129
2 Thermal and crystallinity simulation . . . 130
2.1 Heat equation . . . 130
2.2 Crystallinity content evolution at fusion . . . 131
2.3 Crystallization kinetic model . . . 132
3 Eigenstrain simulation . . . 135
3.1 Thermal expansion . . . 135
3.2 Phase change . . . 136
3.3 Void closure . . . 138
3.4 Residual stress relaxation strain . . . 139
4 Thermomechanical simulation . . . 141
4.1 Thermo-elasticity . . . 141
4.2 Thermo-elasto-plasticity in the recrystallized state . . . 143
5 Conclusions and perspectives . . . 145

8 Finite element analysis of the sintering 147
1 Introduction . . . 149
2 Finite element simulation . . . 149
2.1 Solving strategy . . . 149
2.2 Abaqus user subroutines and other material input data . . . 150
2.3 Mechanical properties . . . 151
3 PTFE plate sintering . . . 151
3.1 Experiment description . . . 151
3.2 Digital image correlation analysis . . . 153
3.3 Infrared thermal camera observation . . . 155
3.4 Comparison with simulation . . . 157
4 Additional experiments . . . 160
4.1 Sintering of inhomogeneous density PTFE plate . . . 160
4.2 Sintering of PTFE compact with defect . . . 162
5 Billet sintering . . . 165
5.1 Sintering of a billet with uniform density . . . 165
5.2 Sintering parameters influence . . . 168

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

5.3 Sintering with density variations 170
6 Conclusions and perspectives 173

Conclusions and perspectives **175**
References 187

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Acknowledgments

Cette thèse aura été pour moi une expérience incroyable durant laquelle j'ai eu l'occasion de rencontrer, de côtoyer et de travailler avec des personnes fantastiques. Je tiens à les remercier très largement.

Merci aux membres de mon jury d'avoir accepté de prendre part à ma soutenance de thèse, et en particulier aux rapporteurs Yann Marco et Olivier Lame d'avoir lu si attentivement mon manuscrit. Merci Sandra Domenek pour ces échanges très intéressants et Lucien Laiarinandrasana d'avoir accepter de présider ce jury.

Nicolas, Gilles et Stéphane, je tiens à vous remercier tous les trois pour votre investissement, pour vos idées formidables et pour ces fameuses réunions toujours très fructueuses. Vous êtes mon trio de directeurs de thèse et j'en suis fier.

Je souhaite remercier Carole et Xavier pour m'avoir fait confiance dès le début en me confiant cette thèse. Merci ensuite à Jean-Yvon de m'avoir si bien encadré à Saint-Gobain, d'avoir pris autant à coeur le sujet et d'avoir fait le lien entre académique et industriel. A Saint Gobain Recherche, j'ai eu l'opportunité de travailler avec certaines personnes que je remercie : Carole, Rémi, Nicolas, Guillaume. Merci aussi à toute l'équipe TMM de m'avoir si bien accueilli. Ce projet n'aurait jamais pu avoir lieu sans l'investissement de certaines personnes chez Saint-Gobain à Willich. Merci Georges, Ansgar, Monika, Lina, André et toute l'équipe qui a toujours été très disponible et surtout à l'écoute pendant trois ans.

Un grand merci aux collègues de mes deux laboratoires ! Merci à tous les amis du LMT et surtout à mes camarades de bureau Myriam, Xuyang, Guillaume, Bhimal, Yanjun ... Merci Rémy, Boubou, Xavier, Marc pour votre aide avec toutes mes expériences. Merci aux amis du PIMM, notamment à mes camarades de bureau et à mes partenaires de foot. Lorsqu'il n'y avait pas d'expérience ou de rendez-vous prévu, c'était toujours difficile de choisir dans quel laboratoire se rendre ! Merci Gaëlle et Vincent pour votre aide sur la DSC et la DRX.

Je remercie aussi toutes les personnes qui m'ont aidé directement sur les expériences. Notamment pour les expériences à l'ESRF, merci à Nathalie, Nils, Isabelle, Sylvie et Sébastien. Pour la compaction isostatique de PTFE, merci Noël et Azziz du LPTMS à Villetaneuse. Merci Matheus, Caiuã et Achraf pour vos stages. Merci Rodrigo pour ces quelques discussions sur le PTFE depuis le Brésil. Merci Nicolas pour ces découpes jet d'eau sur le PTFE compacté.

Enfin, je remercie du fond du coeur mes parents, ma famille et mes amis. J'ai la chance d'être extrêmement entouré et c'est pour moi une grande source de bonheur et de motivation. Merci !

Domitille, merci pour ton soutien démesuré, ta joie de vivre et tant d'autres choses. Ce travail n'aurait pas été le même sans toi.

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Introduction

Polytetrafluoroethylene (PTFE) is a semi-crystalline polymer used in numerous applications in our everyday life. Due to its (extraordinary) specific physico-chemical properties, this polymer is manufactured differently from the other thermoplastics. One of these processes consists in pressing as-polymerized PTFE powder into cylindrical preforms called billets. Pressed PTFE is also reffered to as green PTFE. The billets are later heated above PTFE melting temperature to obtain a "homogeneous" part by erasing interfaces between compacted powder grains. This process stage is called sintering. Sintered PTFE or melt-crystallized PTFE is therefore machined according to its applications.

This work focuses on the sintering of green PTFE and investigates the different mechanisms of deformation that take place. Models are developed for each mechanism in order to be able to simulate the thermomechanical behavior during sintering stage and to determine how to improve the process parameters.

In this introduction, a presentation of PTFE is made in section 1 with its discovery, its principal applications and its synthesis processes. The different manufacturing processes are detailed in section 2. A focus is made on PTFE sintering and the main challenges that it brings. Finally, the structure of the manuscript is presented in section 3.

1 Polytetrafluoroethylene

1.1 Discovery

Polytetrafluoroethylene (PTFE) was discovered by chance by Dr. Roy Plunkett of DuPont Company in 1938 [1]. While seeking for a new fluorinated refrigerant, he realized that the cylinder of tetrafluoroethylene (TFE) he was using had no more pressure in it. When he sawed the cylinder in half to check what was left in it, he found PTFE powder (Figure 1). The discovery of PTFE is a famous example of serendipity.

After several analyses of the white powder, he discovered that it corresponded to PTFE, the linear polymer obtained from TFE. It was then found that PTFE was very slippery, had no flow and was almost chemically inert. Processing methods were designed for PTFE based on metal powder processing. Those methods are still used nowadays, as evidenced by this work which deals with PTFE sintering for industrial applications.

PTFE was then used for the Manhattan project as a corrosion-resistant material to contain Uranium hexafluoride. For those reason, the US government kept the PTFE secret during World War II.

In 1947, DuPont started the commercial production of Teflon® (trademark for PTFE).

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

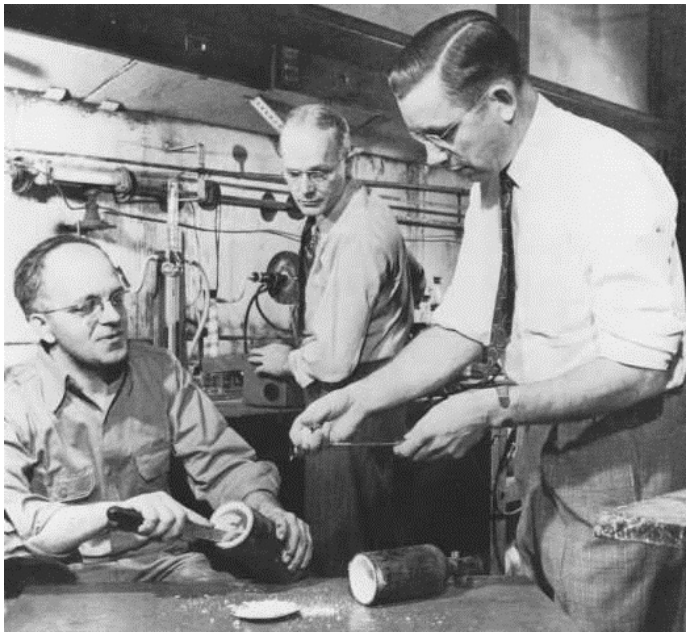


Figure 1: Discovery of PTFE by Dr. Plunkett (on the left) after sawing of the TFE cylinder. Image from the Hagley Museum and Library.

1.2 Properties

PTFE possesses numerous valuable properties. Those are mainly related to the atomic structure of fluorine and of the carbon chains.

Those properties are:

- High melting point [1]
- High thermal stability [1]
- Good mechanical properties at extreme temperatures (low and high)
- Chemical inertness [2, 3]
- Insolubility [3]
- Low coefficient of friction [4]
- Resistance to corrosion [2]
- Hydrophobicity [5]
- Flame resistance [6]
- Good weatherability [1]
- Low dielectric constant / good electrical insulator [1]
- Purity [1]

1.3 Applications

Plenty of industrial application were designed taking advantage of the properties of PTFE [1]. Among them are:

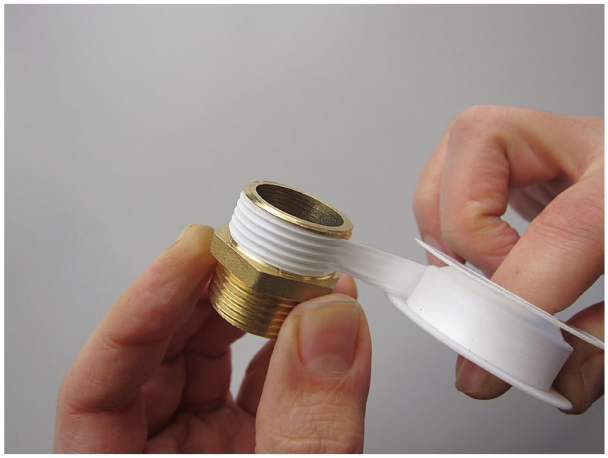
- Bearing (constrains relative movement and reduces the friction between moving parts) shown in Figure 2a
- Seals
- Thread seal tapes shown in Figure 2b

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

- Dry lubricants
- Outdoor application (ex: Gore-Tex®) shown in Figure 2c
- Food container (non stick)
- Coating (against corrosion) shown in Figure 2d
- Paints and inks
- Wire insulation



(a)



(b)



(c)



(d)

Figure 2: Different applications of PTFE: Saint-Gobain Norglide® bearings taken from *bearings.saint-gobain.com* (a), a PTFE thread seal tape taken from *rmmcia.fr* (b), a Gore-Tex jacket taken from *gore-tex.fr* (c) and a frying pan with a PTFE coating taken from *tefal.fr* (d).

1.4 Synthesis

Two commercial polymerization processes of TFE are commonly used: *suspension* polymerization and *emulsion* (or *dispersion*) polymerization.

In the case of *suspension*, TFE is polymerized in water with very small amount of dispersant under vigorous agitation. The dispersant is quickly consumed leading to the

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

PTFE to precipitate.

Granular resins (*fine cut* and *pelletized*) are derived from *suspension*. *Fine cut* resin is usually obtained by milling the raw suspension to obtain particles of size between 20 to 100 µm. This resin has an apparent density below 0.5 g/cm^3. *Pelletized* resin is produced by agglomeration of *fine cut* powder. Therefore, its particle size is usually around 500 µm and has an apparent density above 0.5 g/cm^3. Due to their different flowability, *fine cut* resin is also called *low flow* resin and *pelletized* resin is called *free flow* resin.

In the case of *emulsion*, TFE is polymerized in water with mild agitation and large quantities of dispersant.

PTFE *dispersion* is obtained by concentrating the generated emulsion solution and is used for coatings. *Fine powder* is produced by coagulation, then separation and finally drying of the colloidal particles of the emulsion solution. *Fine powder* is generally used for paste extrusion and is composed of particles around 500 µm in size.

2 Manufacturing process

Traditional thermoplastic manufacturing processes are not used for PTFE because of its extremely high viscosity in the molten state. This is also the case for high density polyethylene that is processed from nascent powders [7].

2.1 Overview of existing processes

Three manufacturing processes of PTFE are predominantly used: compression molding for granular PTFE, extrusion for PTFE fine powder (and granular PTFE), and coating of PTFE dispersion.

Compression molding

Granular PTFE resin is pressed into preforms in a mold at ambient temperature. Those preforms are often called billets which are hollow cylinders. Their diameter usually ranges between 75 to 500 mm and their height between 100 to 1200 mm [1]. They can weigh almost 500 kg. Then the preforms are sintered in ovens to make the PTFE particles coalesce and to remove the porosity originating from compaction.

The sintered billets can be machined to make final parts. They can be skived using a blade by making the billet turn around a mandrill to obtain PTFE films. Those films can reach thicknesses between 50 to 400 µm.

Fillers can be added to the PTFE powder to enhance the mechanical, the wear or other properties of the final product.

Extrusion

Unlike traditional thermoplastic extrusion processes, PTFE paste extrusion is performed with the help of a lubricant [1]. Mixing PTFE fine powder with a lubricant lowers the pressure needed for extrusion. This lubricant is removed after extrusion by evaporation (at a lower temperature than PTFE melting temperature). Other types of extrusion can also be performed such as tube extrusion.

The interest of extrusion is the high strain imposed to the PTFE particles thanks to the different reduction ratios in the extruder. It leads to fibrillation of PTFE particles inside

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

the paste giving rise to some kind of PTFE composite. Its properties can be anisotropic. By this way either the ductility or the stiffness can be increased in one direction.

The extrudate can be sintered or not depending on the desired properties. Thread seal tape is made out of unsintered PTFE tape.

Coating

PTFE coatings can be performed from PTFE dispersion. Coating enables to cover different surfaces and to protect them from corrosion. It is also extensively used for cookwares (Figure 2d) even though the formulation of such coatings is generally more complex with additives and other resins.

2.2 Challenges in the sintering of PTFE compacts

This work is focusing on compression molding of granular PTFE (low flow) and more specifically on the sintering part. During sintering, PTFE preforms are heated in an oven in order to melt the crystals, have the particles coalesce and close the porosity induced by compaction. Due to melting and crystallization, PTFE billets undergo large strains with the temperature evolution. The coupling of those strains with thermal gradients leads to mechanical incompatibilities as illustrated in Figure 3, that generate stresses. In this schematic example, a molten PTFE cylinder crystallizes on the surface creating a "rigid shell". Once the core of the cylinder cools down, it crystallizes as well constraining the "rigid shel". This stress can sometimes lead to damage or even failure of the billets.

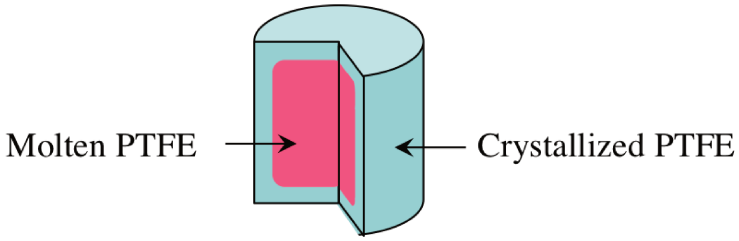


Figure 3: Sketch of a molten PTFE cylinder cooling down. The outer surface crystallizes creating a "rigid shell". Once the core crystallizes as well, it generates stresses by constraining the "rigid shell".

The origins of crack formation in billets are unknown. They could either form at compaction or at sintering. However their opening and probably their propagation are caused by the stresses established during sintering.

At LMT, compaction of PTFE was studied and modeled by Canto [8] and Fredy [9, 10]. Final density gradients were quantified at the end of the compaction by Fredy. Those variations could affect the sintering and be responsible of higher stress levels in the billet.

After sintering, the billets can be skived to obtain PTFE films. Defects can sometimes be observed at this stage.

The objectives of this thesis are to understand the physical mechanisms of deformation occurring in PTFE during the sintering and to be able to model them. The ultimate goal is to predict the state of a PTFE billet during sintering with a thermomechanical simulation using those models.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

3 Structure of the study

The goal is to characterize the different elements necessary to perform a thermomechanical simulation of a PTFE compact sintering. Thus, it is essential to understand the different strain mechanisms that occur during sintering (Chapters 3 to 5) and to characterize the mechanical behavior for PTFE at different temperatures (Chapter 6). The simulation can then be developed using a thermomechanical model that reproduce the different mechanisms of deformation (Chapter 7). A finite element analysis framework is proposed and compared with various experiments (Chapter 8).

The content of each chapter is detailed below.

Chapter 1 - PTFE sintering: state of the art

Two different reviews are presented:

First, the different transitions and microstructural evolution of PTFE are exposed. A focus is made on crystallization mechanisms and crystallization kinetics models.

Second, models and simulations related to sintering of PTFE compacts are summarized.

Chapter 2 - Material and methods

The different experimental methods used during this work are described in this chapter. Differential scanning calorimetry (DSC) method and how to obtain a good baseline from it is explained. Thermomechanical analysis (TMA) technique is presented to measure the eigenstrain during sintering. X-ray diffraction (XRD) techniques and a convenient orientation measurement method is proposed. Then, visualization techniques such as scanning electron microscopy and X-ray microtomography are briefly introduced. Mechanical testings and dynamical mechanical analysis (DMA) are presented too. Finally, digital image correlation (DIC) and infrared spectroscopy techniques used for the analysis of the validation experiment are detailed.

Part I - Thermal uniformity

This part deals with the behavior of PTFE evolving with temperature in the case of thermal uniformity in the part.

Chapter 3 - Green PTFE behavior

Green PTFE compact behavior at heating is studied in this chapter. On top of the thermal expansion and eigenstrain due to melting, an irreversible mechanism due to residual stress relaxation is unveiled.

Chapter 4 - Void closure

In this chapter, the influence of the green PTFE compaction pressure on the initial porosity fraction is characterized. It reveals a void closure mechanism producing an eigenstrain opposed to the strain due to melting.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Chapter 5 - Melt-crystallized PTFE behavior

A singular crystallization kinetics is observed for molten PTFE with two independent crystallization mechanisms. As opposed to green PTFE, melt-crystallized PTFE under thermal cycle shows a more reversible (and isotropic) behavior.

Chapter 6 - Thermomechanical behavior

The mechanical properties of PTFE are investigated as function of temperature. The Young's modulus is measured at different temperatures for green and sintered PTFE. Viscous effects are found to be negligible and molten PTFE features elastomeric elasticity. An elastoplastic behavior is characterized for sintered PTFE.

Part II - Thermal inhomogeneity

This part deals with the behavior of PTFE evolving with temperature in the case of thermal inhomogeneity in the part. The addition of thermal gradient induces stresses inside the part. Thermomechanical simulations can try to evaluate this stress for any thermal loading.

Chapter 7 - Model equations: application to a semi-infinite PTFE part

The different models for the crystallinity kinetics, for the eigenstrain components and for the thermomechanical behavior are detailed and applied in a matlab simulation.

Chapter 8 - Finite element analysis of the sintering

A finite element (FE) method framework is set using the previous models in Abaqus® software. The FE analysis is compared to validation experiments to confirm its results.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Chapter 1

PTFE sintering: state of the art

This chapter contains a state of the art on the microstructural evolution of PTFE during sintering and of the elements of modeling needed to perform a thermomechanical simulation of PTFE sintering.

Contents

1 Microstructural evolution of PTFE during sintering 22

1.1 Phase transitions 22

1.2 Crystalline lamellae formation and growth 24

1.3 Crystallization kinetics 27

2 Mechanical analysis of PTFE sintering 32

2.1 Mechanical behavior of PTFE during sintering 32

2.2 Simulation of PTFE sintering 36

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

1 Microstructural evolution of PTFE during sintering

Polytetrafluoroethylene is subject to various microstructural modifications during sintering. Phase changes and glass transition have an impact on the final state of a sintered PTFE part. Melting and crystallization represent the most important phase change during sintering. Crystallinity and crystalline morphology are expected to evolve during these transitions. This section lists the different transitions likely to occur during the sintering cycle, then presents different observations on the evolution of crystallites during crystallization and finally exposes crystallization kinetic models of PTFE described in the literature.

1.1 Phase transitions

PTFE is a semi-crystalline polymer which means that part of its molecular chains are strictly organized into a crystal. For nascent PTFE powders, the crystallinity content can reach more than 90% and for sintered PTFE is usually around 50%. The crystallinity content refers to the fraction of ordered segments compared to the totality and is expressed here in mass fraction. The less ordered fraction is called amorphous phase as opposed to the crystalline structure.

The crystalline phase is subject to changes as function of temperature and pressure variations. The phase diagram of PTFE is presented in Figure 1.1 [11]. Four crystallines phases are known for PTFE and their structure is detailed in Figure 1.2. A double transition occurs around ambient temperature, from Triclinic phase II to Hexagonal phase IV above 19°C, and from Hexagonal phase IV to Pseudo-hexagonal phase I at 30°C [12]. Above 340°C, the crystal organization vanishes and the entire polymer becomes amorphous. This transition is called melting at heating and crystallization at cooling.

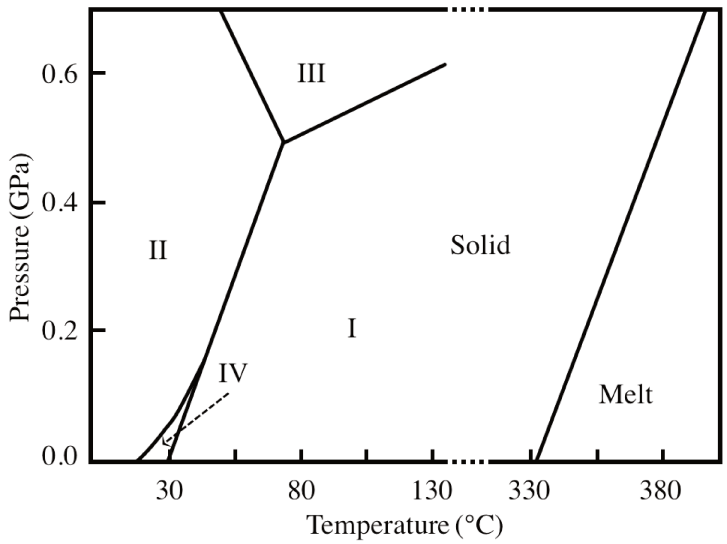


Figure 1.1: PTFE phase diagram. Based on [11].

At higher pressures (above 0.5 GPa), crystalline structure change from Hexagonal (or Triclinic) to Orthorhombic [13] (Figure 1.2). The crystalline transitions between phase II and phase IV, and between phase IV and phase I do not correspond to significant microstructural modification. The helical conformation of phase II is untwisted from 13 atoms per full turn to 15 atoms per full turn in phase IV and I [14]. Phase I is more mobile

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

than phase IV, and allows more angular motions (torsion) around the chain [15, 16].

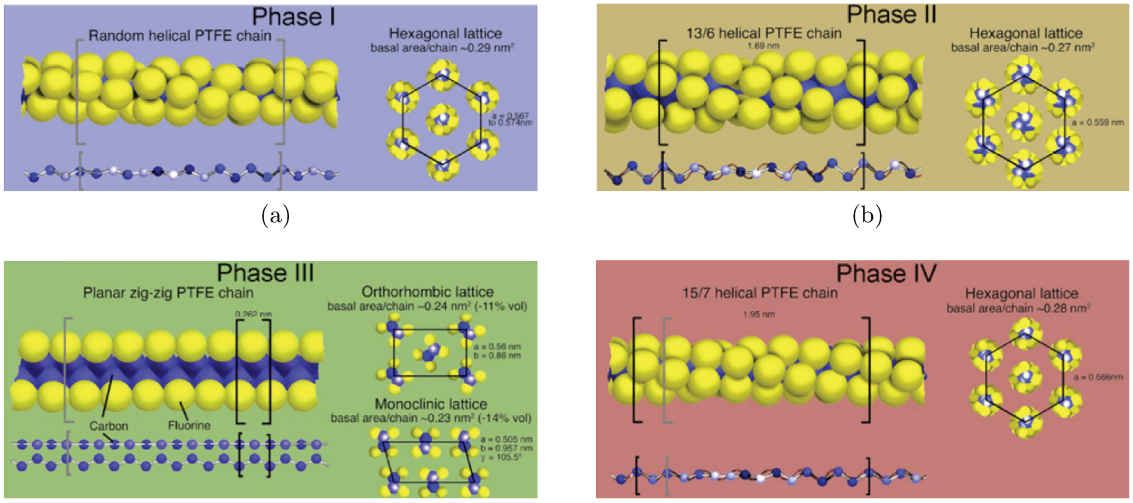


Figure 1.2: PTFE crystalline phases. Taken from [13].

PTFE chains are extremely long (about 20 µm) due to the high molecular weight (around 10^7 g/mol). This limits substantially the mobility of the polymer chains and therefore their ability to reorganize at phase changes. Torsion along the carbon chain remains the favorite possibility for reorganization. Conformational defects can move thanks to an helix reversal mechanism [17, 18]. PTFE chains being an helix, two chiral configurations exists (L and R). Switching from one to another within the same chain allows to reorganize the chains to form crystals. Illustrations of the different configurations and how the defects can move are presented in Figure 1.3. Figure 1.3c underlines that a crystal can only exist within same configuration L or R.

The other important transition in semi-crystalline polymers is the glass transition which concerns the amorphous phase[19]. The material is considered vitrous below the glass transition temperature (T_g) and in rubbery state above. In the rubbery state, the molecular chains in the amorphous phase presents a high mobility which decreases the viscosity of the material. The ductility is usually much higher and the stress is only carried by the entanglements between chains. In the vitrous state, the molecular chains have low mobility which makes the material more fragile.

In the case of PTFE, the exact position of the glass transition has long been and is still a subject of debate. Three transitions can be observed using dynamic mechanical analysis (DMA) tests (see Figure 1.4). The γ and α-transitions are related to the amorphous phase. The β-transition characterizes the double crystalline transition at ambient temperature. Some considers that the glass transition is the γ-transition around -110°C [20, 21] and others that it is the α-transition around 130°C [22, 23, 24, 25, 26].

More recent studies suggest that both γ and α transitions are related to two morphologies of amorphous phase: the rigid amorphous fraction (RAF) and the mobile amorphous fraction (MAF) shown in Figure 1.5. The RAF is the part of the amorphous phase at the vicinity of the crystalline phase. Conversely, the MAF is a fraction of the amorphous phase further away from the crystalline phase and therefore more mobile as less impacted by the crystals. The γ-transition corresponds to the glass transition of the MAF around -110°C and the α-transition corresponds to the glass transition of the RAF around 130°C [28, 27].

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

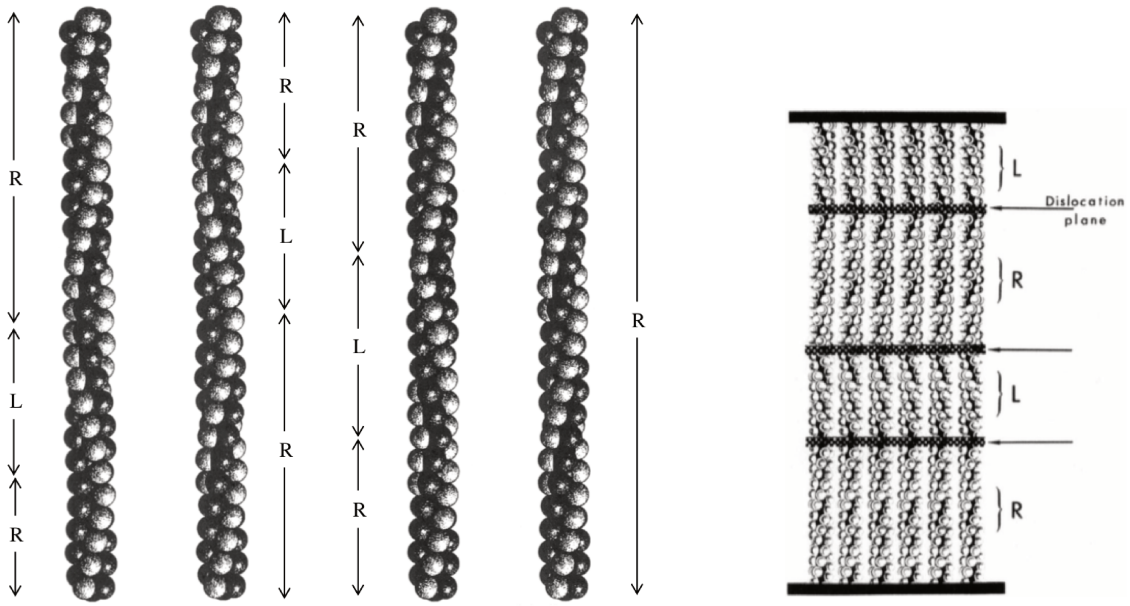


Figure 1.3: Illustration of helix configuration L and R in the same chain. A defect (configuration change) moves along a chain without changing the overall chain torsion (a). A defect can be created without changing the overall chain torsion (b). Taken from [17]. Crystals are formed with chains in the same configuration (c). Taken from [16].

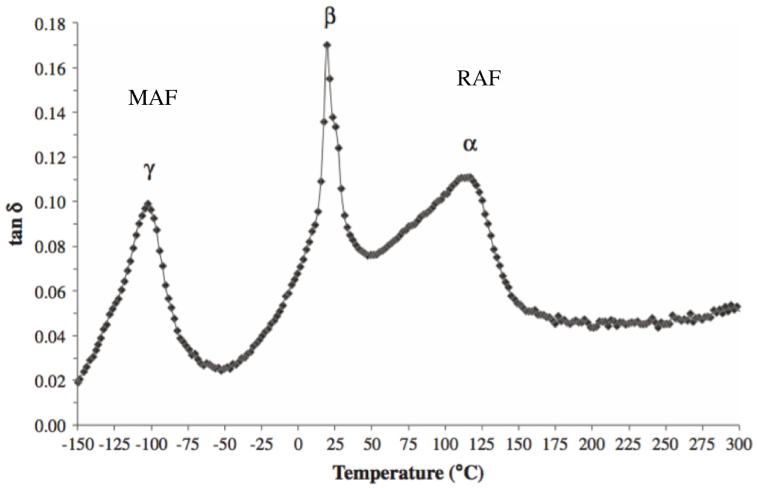


Figure 1.4: $\tan\delta$ obtained with DMA experiment. The γ, β and α-transitions are observed with the different local maxima of $\tan\delta$. Taken from [27].

1.2 Crystalline lamellae formation and growth

Nascent PTFE is almost fully crystalline due to crystallization during polymerization. Extended-chain crystals are formed in these conditions [29, 30]. Figure 1.6 presents the difference between extended-chain crystals and folded-chain crystals. The former consists in stacks of chains or folded chains with a length between fold above 2 000 Å according to Wunderlich's definition [29] (Figure 1.6a). The latter is a stack of folded chains with a

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

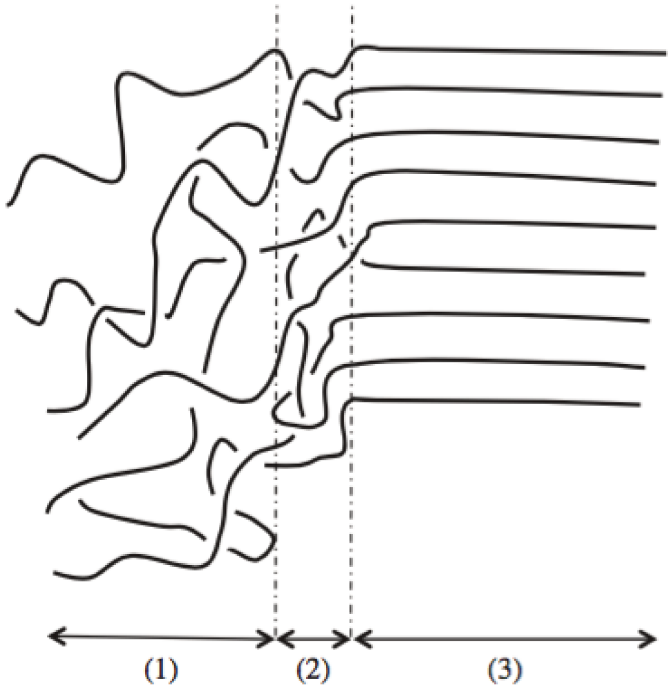


Figure 1.5: Sketch of PTFE semi-crystalline structure. (1) corresponds to the mobile amorphous fraction (MAF), (2) to the rigid amorphous fraction (RAF) and (3) to the crystalline phase. Taken from [27].

length between fold lower than 2 000 Å (Figure 1.6b). The distance between folds is the crystal lamellae thickness. It was shown by Geil et al. [31] that nascent particles are often folds of PTFE chains with a large lamellae thickness (above 2 000 Å).

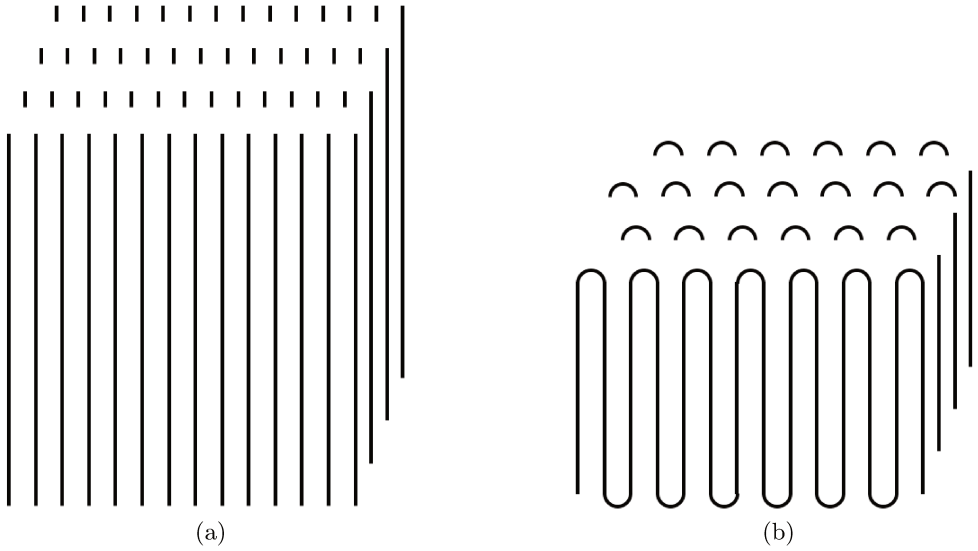


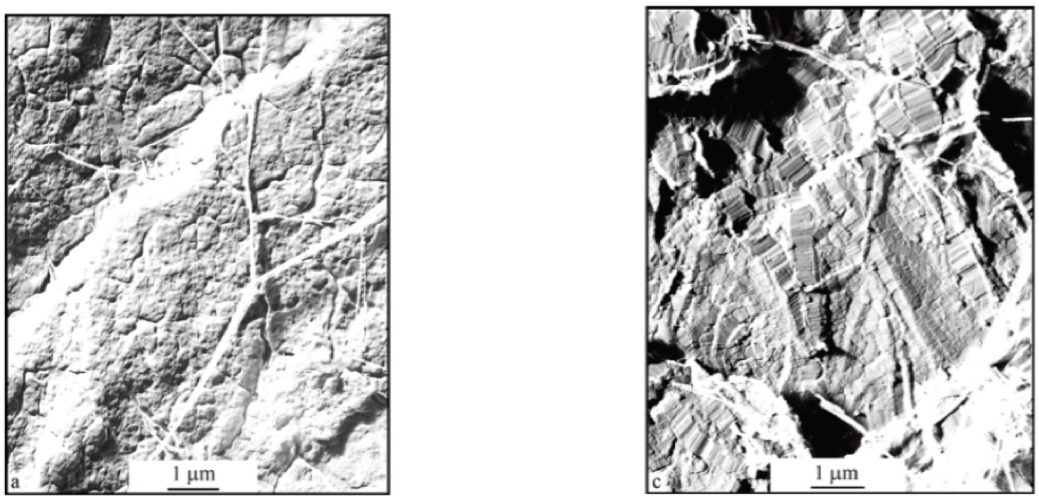
Figure 1.6: Sketch of an extended-chain crystal (a) and a folded-chain crystal (b).

During melting, PTFE chains lose their crystal organization and form a mesomorphic melt. The mesomorphic melt is a pseudo-structured state from which originates the future

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

crystals. According to Geil et al. [31], the chains start to reorganize and fold in the melt. Therefore, the time spent in the melt is important for the subsequent crystallization.

During the cooling of the melt, PTFE recrystallizes and form folded-chain crystals. Those lamellae can be observed via scanning electron microscopy (SEM) techniques as shown in Figure 1.7.



(a) (b)

Figure 1.7: SEM micrographs of sintered PTFE at 350°C for 10 min and quenched into water (a) and of sintered PTFE at 350°C for 30 min and slow cooled (b). Images taken from [31].

The temperature history at cooling seem has a pronounced effect on the crystal perfection and notably on the lamellae thickness (see Figure 1.7). Different studies observed this effect via SEM [32, 31, 30]. Figure 1.8 exposes this dependency from statistical analyses based on SEM micrographs. A clear increase of the lamellae thickness is shown as function of the temperature between 312 and 322°C (Figure 1.8a), as well as an increase with time spent at these temperature (Figure 1.8b).

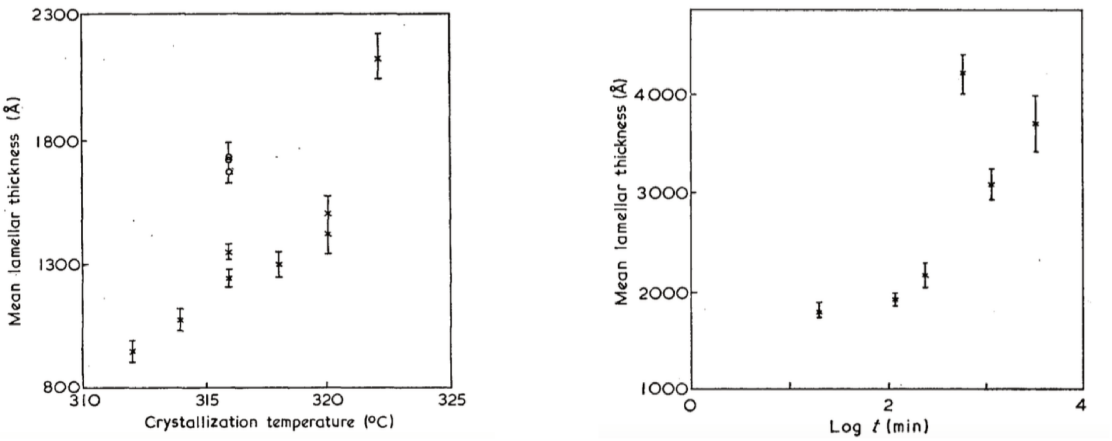
The same tendency was obtained using differential scanning calorimetry (DSC) and X-ray scattering measurements [33]. Melting peak in DSC gives information on the lamellae size distribution thanks to Gibbs-Thomson equation [34, 35]:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_f l}\right) \tag{1.1}$$

where T_m is the melting temperature of the crystal, T_m^0 is the melting temperature of an infinite crystal, σ_e is the end surface free energy, Δh_f is the enthalpy of fusion per unit volume of crystal and l is the lamellae thickness.

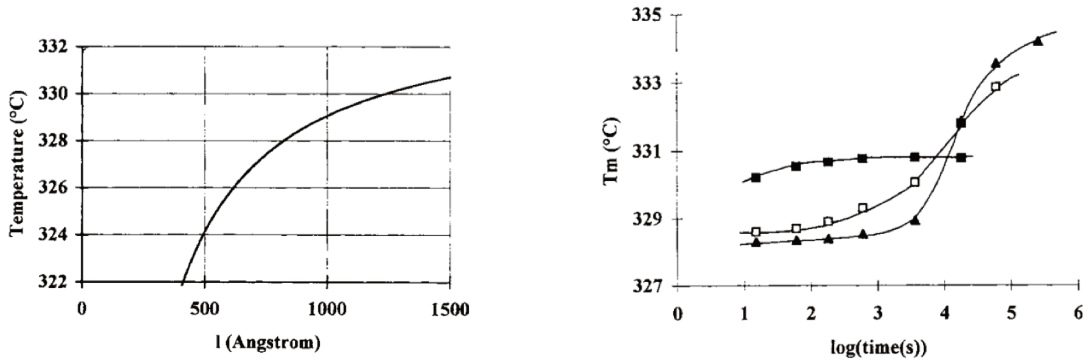
Thanks to DSC analysis, this equation leads to a relation between melting temperature and crystallite size (Figure 1.9a). Therefore the lamellae thickness can be directly accessed from DSC measurements via the melting temperature. Figure 1.9b gives the melting temperature as function of the crystallization time for different temperatures. It appears that the evolution of the lamellae thickness with time is dependent on the crystallization temperature. This lead Ferry et al. [33] to conclude that at high temperature crystal perfection is more likely to happen due to higher thermal agitation. Conversely, at lower temperature viscosity increases leading to thinner lamellae.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles



(a) (b)

Figure 1.8: Lamellae thickness as function of crystallization temperature for 20 min isotherm (a) and as function of crystallization time at 322°C (b). These results were obtained by Bassett [32] from SEM observations.



(a) (b)

Figure 1.9: Melting temperature as function of lamellae thickness (a) and temperature of the maximum of DSC melting peak as function of crystallization time, for different temperatures: 315°C (■), 320°C (□) and 323°C (▲) (b). Images taken from [33].

1.3 Crystallization kinetics

As previously shown with the evolution of the crystalline lamellae, the crystallization follows a specific kinetic law. It describes the evolution of the crystallinity content with temperature and time.

Crystallization kinetic models usually deal with competition between nucleation and growth of the crystals. Close to melting temperature, the nucleation is low as the probability to create a nuclei is almost equal to the probability to that a nuclei is removed. When the temperature decreases, the growth of the crystal is more favorable as the mobility of the chains is important. At even lower temperature, the nucleation becomes more important and the mobility is reduced.

The crystallization kinetics of polymers is often modeled with classical models. However it is very common to encounter a secondary crystallization mechanism which complicates

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

its modeling.

Avrami model

The most known model for crystallization kinetic is the Avrami model which describes spherulitic crystal nucleation and growth [36, 37, 38]. The Avrami model is relevant for isothermal crystallization and has been widely applied for metals and polymers crystallization. The Avrami equation estimates the relative crystallinity content $\alpha = \chi/\chi^{\infty}$ where χ is the crystalline mass fraction and χ^{∞} the crystalline mass fraction at the end of an isothermal crystallization:

$$\alpha(t) = 1 - \exp\left(-K\ t^n\right) \tag{1.2}$$

where $K(T)$ is the Avrami kinetic constant which depends on the isothermal temperature T and n is the Avrami exponent which characterizes both the growth dimension and the nucleation type (instantaneous or sporadic). The parameter n is a positive integer between 1 and 4. It is equal to the growth dimension for an instantaneous nucleation and to the growth dimension + 1 for a sporadic nucleation. For example, $n = 1$ corresponds to an instantaneous nucleation with a linear growth, and $n = 4$ to a sporadic nucleation with growth in the three dimensions.

The Avrami model relies on several assumptions:

- uniform nucleation;
- no volume change during transformation;
- complete transformation;
- constant growth rate during the transformation.

Ozawa model - constant cooling rates

Ozawa extended the Avrami model to anisothermal crystallization in the case of a constant cooling rate. This model is very convenient to analyze anisothermal DSC experiments. Those experiments are mandatory when the crystallization is fast and it is not possible to perform isotherms without initiating the crystallization. The equation of the Ozawa model [39] is defined as

$$\alpha(T) = 1 - \exp\left(-\frac{k(T)}{\phi^n}\right) \tag{1.3}$$

where $k(T)$ is the Ozawa kinetic constant and ϕ is the cooling rate.

The Ozawa model relies on the additional *isokinetic* hypothesis. It implies that the growth rate G and the nucleation rate $\dot{N}$ follow the same temperature evolution.

The Ozawa kinetic constant $k(T)$ is related to the Avrami kinetic constant $K(T)$ by the following equation:

$$K = \left(\frac{\mathrm{d}k^{1/n}}{\mathrm{d}T}\right)^n \tag{1.4}$$

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Nakamura model - indifferent thermal history

Nakamura extended the Avrami model to any thermal history. This model is essential to simulate the evolution of the crystallinity content for a complex thermal loading such as the one observed by PTFE in a billet during sintering. The equation of Nakamura model [40] is

$$\alpha(t) = 1 - \exp\left(-\left\{\int_0^t \kappa\big(T(\tau)\big)\mathrm{d}\tau\right\}^n\right) \tag{1.5}$$

where κ is Nakamura kinetic constant and is related to the other kinetic constants via

$$\kappa = K^{1/n} = \frac{\mathrm{d}k^{1/n}}{\mathrm{d}T} \tag{1.6}$$

It can also be expressed using the differential expression which is more convenient for incremental computations

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = n\ \kappa\big(T(t)\big)\left\{\int_0^t \kappa\big(T(\tau)\big)\mathrm{d}\tau\right\}^{n-1}(1-\alpha) \tag{1.7}$$

Kinetic constant evolution

Hoffman and Lauritzen proposed an expression for the growth rate G [34] as function of the temperature

$$G(T) = G_0 \exp\left(-\frac{U^*}{R(T-T_\infty)}\right)\exp\left(-\frac{K_g}{T\Delta T f}\right) \tag{1.8}$$

where G_0 is a constant, U^* is the activation energy for macromolecules movement (usually ranging between 4000−7000 J/mol [34, 41]), R is the gas constant and K_g is a parameter associated to nucleation. T_∞ is a temperature where any macromolecular movement is forbidden, and usually $T_\infty = T_g - 30$, where T_g is the glass transition temperature. $\Delta T = T_m^0 - T$ where T_m^0 is the melting temperature of an infinite crystal and f is defined by $f = 2T/(T_m^0 + T)$.

The first exponential term $\exp\left(-U^*/R(T-T_\infty)\right)$ conveys the diffusion process of the chains in the molten state. The further above T_∞ the temperature T, the higher the diffusion. The second exponential term $\exp\left(-K_g/T\Delta T f\right)$ is related to the nucleation at the surface of the crystalline lamella. The further below T_m the temperature, the faster the growth of the lamella. Those two terms balance each other producing a temperature function similar to an asymmetric Gaussian.

The same type of temperature evolution is generally chosen to characterize the kinetic constant $K(T)$ [42, 43, 44]. An illustration of the kinetic constant as function of temperature is proposed in Figure 1.10.

Secondary crystallization kinetics

Secondary crystallization mechanisms are also a very common feature in polymers [45, 46, 47, 48, 49]. Some models exist to try to capture the overall kinetics. Verhoyen proposed the *consecutive* Avrami model [50] which sums up to independent crystallization kinetics. The equation of the *consecutive* Avrami model is

$$\alpha(t) = w_1\big(1 - \exp\left(-K_1(t-t_{i1})^{n_1}\right)\big) + w_2\big(1 - \exp\left(-K_2(t-t_{i2})^{n_2}\right)\big) \tag{1.9}$$

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

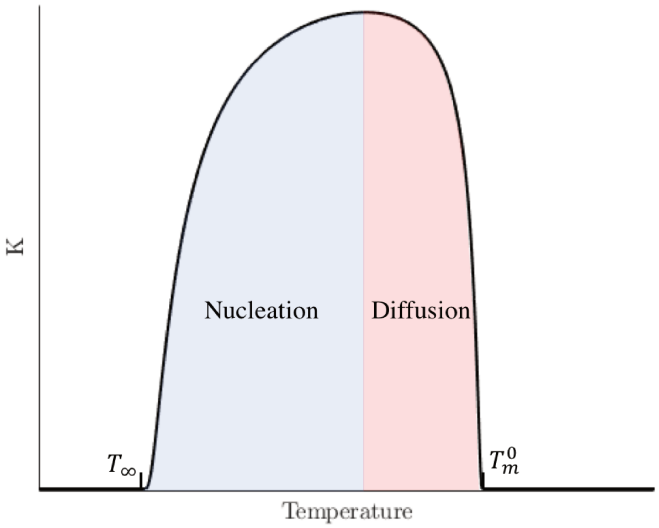


Figure 1.10: Illustration of the kinetic constant as function of temperature. The shape of the function is given by (1.8). The high temperature region is governed by the diffusion process and the low temperature region is governed by nucleation.

where w_1 and w_2 are weight factors related to each crystallization, K_1, K_2, n_1 and n_2 are respectively the Avrami kinetic constants and the Avrami exponents for each crystallization. t_{i1} and t_{i2} are the induction times respectively for the primary and the secondary crystallization.

The *consecutive* Avrami model is the extension of the *parallel* Avrami model introduced by Velisaris [51] with the addition of induction times. The inductions times (t_{i1} and t_{i2}) delay the start the primary and the secondary crystallization.

The secondary crystallization is usually a phenomenon that starts later and that is dependent on the primary crystallization. The Hillier model proposes to model the secondary crystallization kinetic with a convolution to the primary crystallization kinetic [52]. For that reason, the Hillier model is based on more physical assumptions than the consecutive Avrami model. The Hillier model can be written as:

$$\alpha(t) = w_1\big(1-\exp\left(-K_1 t^{n_1}\right)\big) + w_2 \int_0^t \frac{\partial}{\partial t}\Big(1-\exp\left(-K_1 \tau^{n_1}\right)\Big)\big[1-\exp\left(-K_2(t-\tau)\right)\big]\mathrm{d}\tau \tag{1.10}$$

In this model is that the secondary crystallization occurs in a domain linked to the primary crystallized domain. Such evolution is relevant in the case of lamellar thickening or in the case of interlamellar crystallization. The Hillier model is nevertheless usually more difficult to handle for experimental data fitting. For that reason, this model is less frequently used.

Those two models were presented for the isothermal case and can be extended to non-isothermal kinetics using Nakamura's formalism.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

PTFE crystallization kinetics

PTFE crystallization kinetics via DSC experiments was first studied by Ozawa in 1981 [53] and later by Seo and by Wang et al. [54, 55]. Figure 1.11 shows the evolution of the relative crystallinity as function of the temperature for different cooling rates. As mentioned previously, the PTFE is shown to crystallize very quickly on a narrow temperature range (between 320°C and 300°C). The authors found out that the Avrami exponent n is close to 1 (1.5 in the case of Wang). It means that the crystallization has a linear growth with an instantaneous nucleation. This result is consistent with observations made by Symons [56] on linear growth crystallization using SEM observations. Ozawa mentioned that secondary crystallization could exist in PTFE and have an impact on the final crystallinity content.

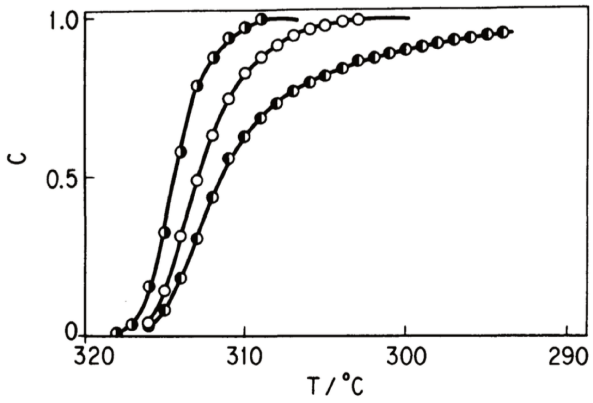


Figure 1.11: Relative crystallinity α as function of the temperature for different cooling rates: 0.9°C/min (◑), 2.9°C/min (○) and 4.5°C/min (◐). Image taken from [53].

Recent studies and perspectives

A more recent work explored crystallization of PTFE over a wide range of cooling rates using ultra fast scanning calorimetry (UFSC). UFSC allowed to reach cooling rates up to 800 000°C/s. The study showed it was impossible to prevent crystallization to happen even at very high cooling rates [57].

Others studies pointed out a reversible behavior during crystallization and second melting of PTFE (i.e. melting of melt-crystallized PTFE) [58, 59]. Figure 1.12 shows a DSC measurement performed by the authors. On the calorigram, it can be seen that the crystallization peak and second melting peak are spread over a broad temperature range. Using temperature modulated DSC (TMDSC), the authors found that the behavior between 220 and 310°C is reversible. The TMDSC revealed an "excess" of specific heat capacity that could be related to a reversible melting phenomenon.

The limitation of the Avrami/Nakamura model for the application to PTFE comes from the fact that the transformation is not always complete. The final crystallinity content of PTFE depends on the thermal history. In the different articles studying PTFE crystallization kinetics, the final value of α was set to 1 whereas χ^{∞} varies with cooling rates. It would be valuable to take this evolution into account within the kinetic model.

The recent studies showed a crystallization behavior between 220 and 310°C which was not integrated to any crystallization kinetic model. Therefore it would be interesting to consider this evolution in a model to truly appreciate the crystallinity content variation.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

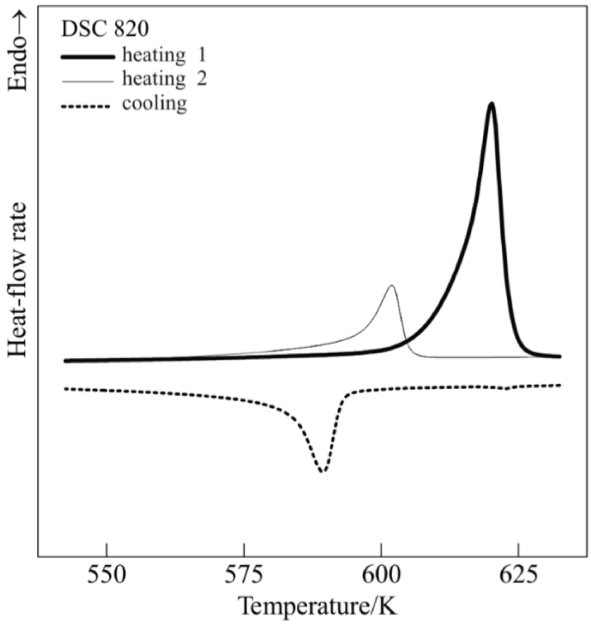


Figure 1.12: DSC calorigram obtained from nascent PTFE melted a first time, cooled down and melted a second time. The heating rate is 20°C/min and the cooling rate is 10 °C/min. The crystallization peak and secondary melting peak seems to extend on a broad temperature region. Figure taken from [59].

2 Mechanical analysis of PTFE sintering

This section reports the different elements from the literature necessary to establish a simulation of the sintering of PTFE. First mechanical properties for PTFE are exposed and then a list of different existing models and simulations are proposed.

2.1 Mechanical behavior of PTFE during sintering

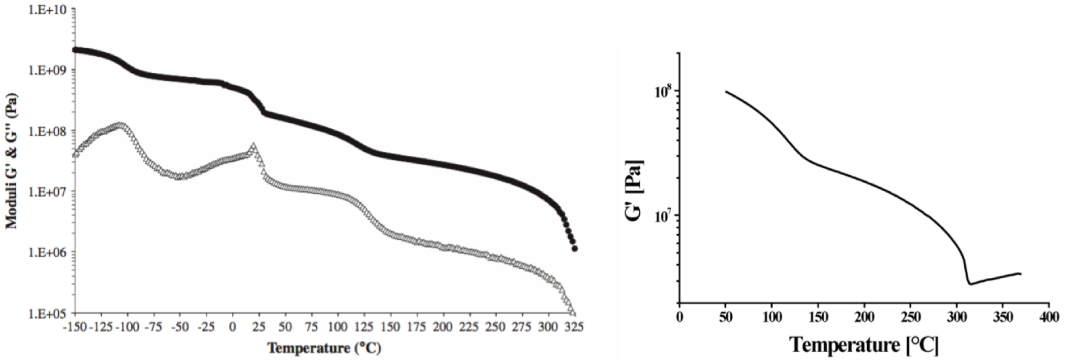
Mechanical properties of sintered PTFE

Only a few papers exist on mechanical properties of PTFE. PTFE is known as being a polymer having quite low mechanical properties. Therefore it often needs to be enhanced by filler addition.

PTFE has a very high viscosity η in the molten state: 10^{11}–10^{12} Poise at 380°C [1]. Therefore it does not flow in the molten state. From DMA experiments shown in Figure 1.13a, the loss modulus (G") is always at least one magnitude order below the storage modulus (G'). It means that the material behaves as an elastic material at the frequency studied with very a short relaxation time.

Other authors studied the evolution of the Young's (E) modulus as function of temperature (Figure 1.14). Some results were obtained from tensile tests [61, 62] and others from compression tests [63]. The evolution of E is consistent when comparing between the different results. Young's modulus presents a slope discontinuity around 100° C which may be related to the α-transition. The same slope discontinuity can be observed in the DMA measurements from Figure 6.1. Besides, the evolution of E with the temperature can be

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles



(a) (b)

Figure 1.13: Dynamic mechanical analysis of sintered PTFE in torsion. Storage modulus (■) and loss modulus obtained (△) at 1 rad/s (a) and storage modulus up to 370°C at 1 Hz (b). Image (a) taken from [27] and (b) from [60].

obtained from the evolution of the shear modulus (G) using the relation:

$$G = \frac{E}{2(1+\nu)} \tag{1.11}$$

where ν is the Poisson's ratio. This relation is valid for an isotropic material.

Poisson's ratio for PTFE is between 0.40-0.46 [62, 63, 1], and no mention of a variation with temperature is made. Therefore, the Young's modulus evolution obtained from the storage modulus (G') is consistent with Figure 1.14.

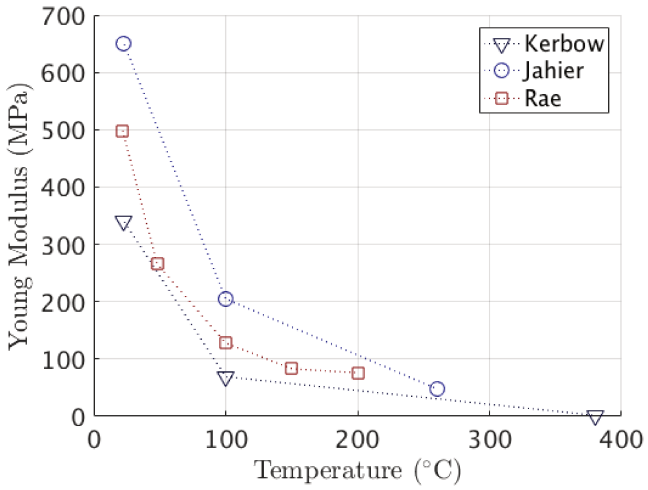


Figure 1.14: Young modulus of sintered PTFE obtained by different authors from tensile tests [61, 62] and from compression tests [63].

Crystal plasticity is an important deformation mechanism in PTFE. Crystalline planes slides against each other at a low energy cost. Thus, the crystal shear plasticity threshold is very low [64, 65]. It explains the low coefficient of friction of PTFE and the tendency of

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

PTFE crystals to form fibrils under shear [66, 67].

Sintered PTFE yield stress evolution with temperature has been investigated by several authors via tensile tests or compression tests [61, 68]. Figure 1.15 gathers those results in one graph. The evolution of the yield stress with temperature seems similar to the evolution of Young's modulus. In particular, the same slope discontinuity seems to be observed below 100° C which could correspond to the α-transition (glass transition of the RAF).

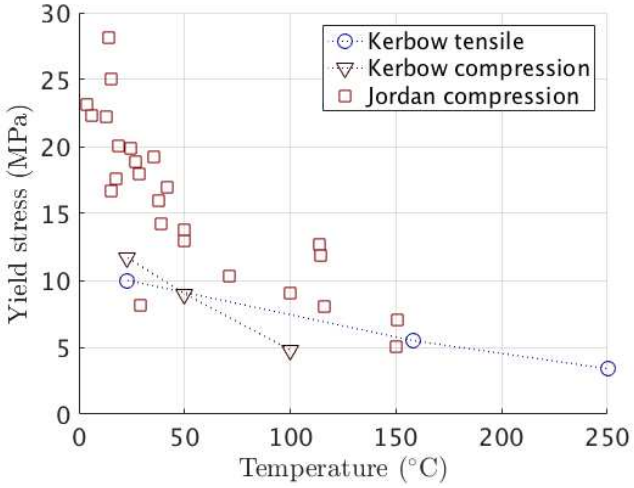


Figure 1.15: Yield stress of sintered PTFE as function of temperature measured by different authors: Kerbow et al. from tensile and compression tests [61], Jordan et al. from compression tests [68].

Mechanical models for PTFE

Some authors modeled the thermomechanical behavior of PTFE [69, 70]. They all decompose the behavior into two terms, one viscoelastic component and one viscoplastic component. In other words, a part of the strain is reversible, another is irreversible and both are time-dependent. A representation of the models used to describe behavior PTFE is shown in Figure 1.16.

Similarly Bergström modeled the thermomechanical behavior of PTFE with fillers for large strains using the Dual Network Fluoropolymer model [71]. This model was used to simulate the viscoelastic behavior and the viscoplastic behavior corresponding to irreversible chain sliding. The viscoelastic behavior is described by a combination of short term and long term relaxations. This model has been tuned using a set of specific experiments up to 200°C (uniaxial tension tests, uniaxial compression tests, volumetric compression tests and multiaxial small punch tests).

Mechanical properties of green PTFE after compaction

PTFE powder compaction 3D-behavior has been characterized by Canto [8] and Fredy et al. [9, 10] at room temperature using a triaxial machine. A Drucker-Prager/cap model was used to describe the mechanical behavior of PTFE during compaction. The mechanical properties of PTFE have been identified for different void ratios e (i.e. different levels of

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

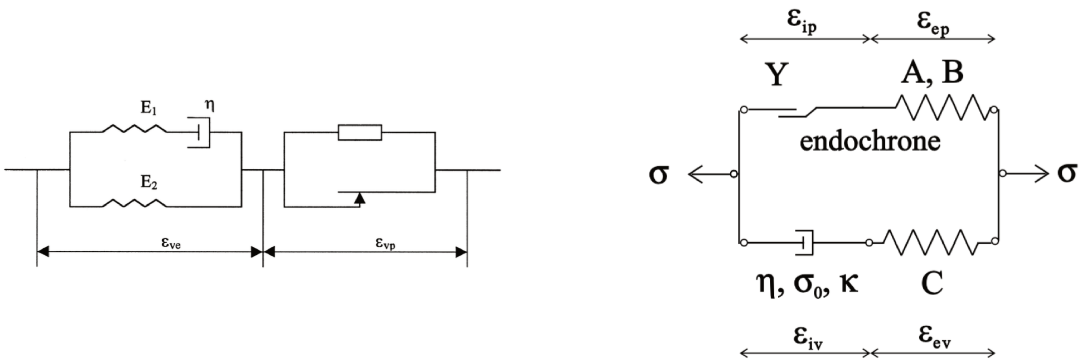
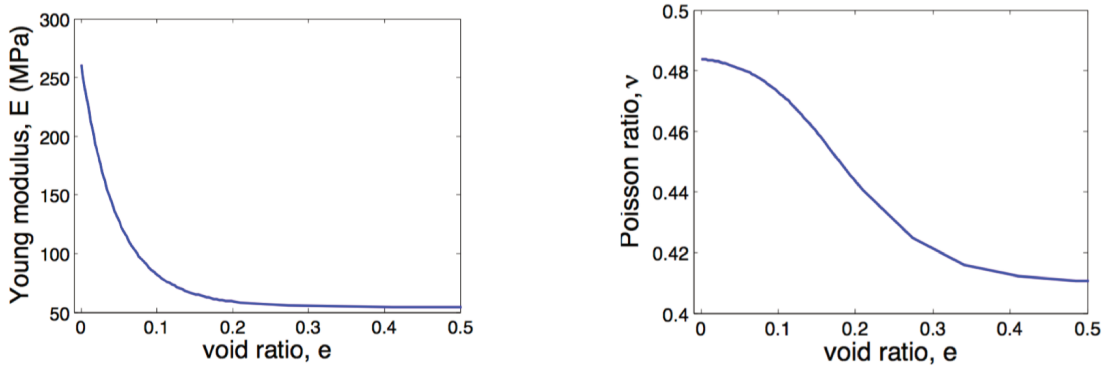


Figure 1.16: Representation of the rheological models used to describe behavior of PTFE. (a) from [69] and (b) from [70].

compaction) in order to complete this type of finite element simulations. The void ratio e is ratio between the volume of the voids and the volume of the solids, and is related to the porosity n by $e = n/(1-n)$. Figure 1.17 shows the evolution of Young's modulus and of Poisson's ratio as functions of the void ratio. It gives the evolution of the mechanichal properties during the compaction step. These results are particularly interesting when looking for the properties of PTFE compacts obtained from different compaction levels.



(a) (b)

Figure 1.17: Evolution of Young's modulus (a) and Poisson's ratio (b) as function of the void ratio for compacted PTFE powder. Results obtained from a hydrostatic test. Figures taken from [10].

Results from compaction simulation are useful for the simulation of the sintering step. Figure 1.18 shows the density distributions along the height of the green PTFE billet obtained for different compaction pressures. In particular, density distributions after compaction can be an input for refined sintering simulations. Due to the different mechanical response for different void ratios, it is very likely that density gradient modifies the stress state in PTFE billets during sintering.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

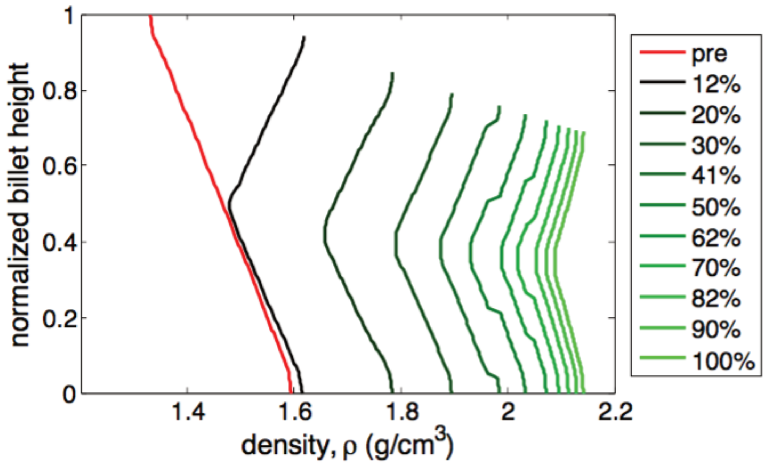


Figure 1.18: Density distributions along the eight of the PTFE billet after compaction. The density profiles are plotted for percentages of the maximal applied stress. Figure taken from [10].

2.2 Simulation of PTFE sintering

Strain mechanisms during sintering and model

A study by Canto [8, 72] investigated the deformation mechanisms during the sintering of cold-pressed PTFE compacts. Dilatometric experiments (or thermomechanical analysis) were performed on small PTFE compacts. The material used was a free flow resin. Both isostatic compaction and uniaxial compaction were studied.

The classical strain mechanisms during sintering are the thermal expansion and the strain caused by phase changes (melting and crystallization for PTFE). Figure 1.19 shows the measured thermal strain obtained for a uniaxial cold compact during sintering. It appears that the strain is anisotropic: the uniaxial compaction induced a transverse isotropic behavior.

An additional strain related to void closure was observed as shown in Figure 1.20 for an isotropically compacted sample. The subtraction of the strain of a sample without porosity to the strain of an initially porous sample reveals the existence of a void closure strain ε^{vc}. This shrinkage starts at melting. The void closure evolution are usually modeled considering surface tension and viscous behavior of the material [73]. In this article, a phenomenological model has been proposed:

$$\varepsilon^{vc} = \Delta\varepsilon^{vc}_{max}\left[1 - \exp(-a_{vc}t)\right] \quad H\big(T(t) - T_m\big) \tag{1.12}$$

with a temporal parameter a_{vc} and the strain related to the full closure of the porosity $\Delta\varepsilon^{vc}_{max}$ and H the Heaviside function.

Another effect was observed at heating corresponding to a "recovery" phenomenon. This effect is illustrated on Figure 1.21 where successive thermal cycle with increasing maximal temperature are performed on a uniaxially compacted sample. It appears that after the first cycles, the a permanent strain is observed. This strain corresponds to an expansion in the compaction direction and to a shrinkage in the transverse direction. The "recovery" is supposed to be related to the uniaxial pressing.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

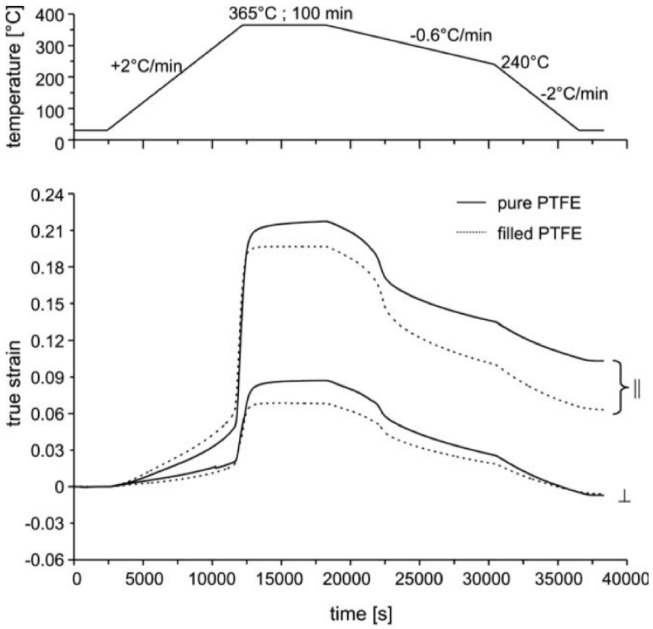


Figure 1.19: Thermal cycle and corresponding strain obtained from TMA experiment in compaction direction (∥) and in transverse direction (⊥). Figure taken from Canto [72].

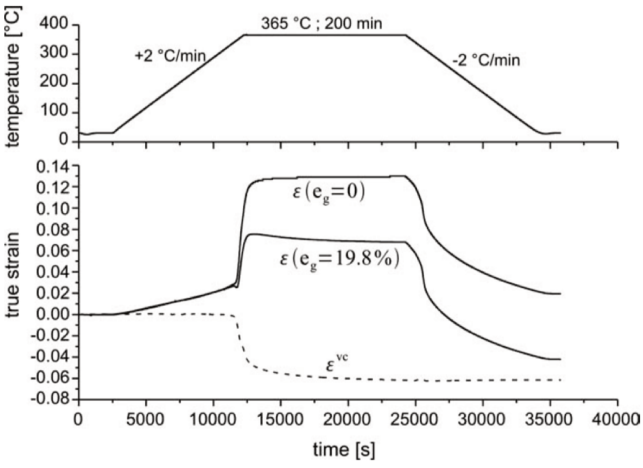


Figure 1.20: Thermal cycle and corresponding strain obtained from TMA experiment for two PTFE samples with different void ratios (i.e. different initial compactions). The subtraction of the two curves gives an evaluation of the strain related to void closure. Figure taken from Canto [72].

Finite element analysis

A mere finite element method analysis of the billet sintering is proposed by Andena [60]. The DSC, dilatometric results evolution of Young's modulus with temperature are taken as input for the simulation. The billet is represented with an asymmetric geometry.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

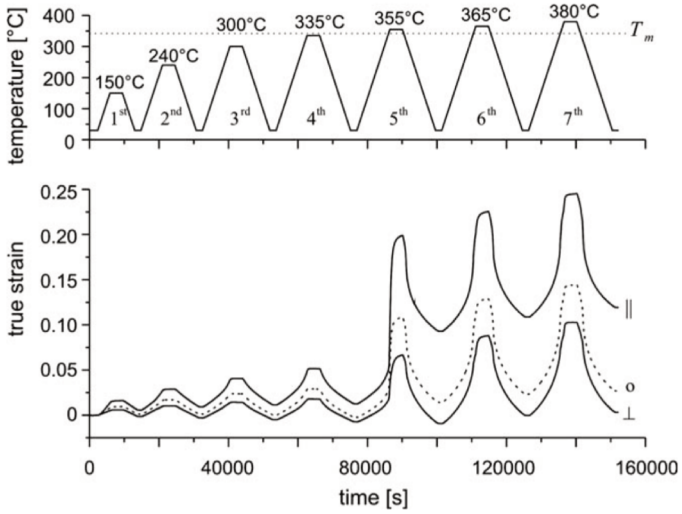


Figure 1.21: Thermal cycles with increasing maximal temperature and corresponding strain obtained from TMA experiment in compaction direction (∥), in transverse direction (⊥) and for an isotropic specimen. Figure taken from Canto[72].

First, the thermal simulation is done by computing the heat equation:

$$\rho c_p \frac{\partial T}{\partial t} + \nabla \left(-k \nabla T\right) = r \tag{1.13}$$

where ρ is the density, c_p is the specific heat, T the temperature, k is the thermal conductivity and r the heat source.

The values of the specific heat c_p are taken from the DSC measurements and its evolution with temperature is such that it incorporates the latent heats of fusion and crystallization. Therefore r is considered as null in the equation (1.13). The conductivity k is chosen linear with temperature.

Second, the thermal expansion coefficient is fitted from thermomechanichal analysis (TMA) experiments made on small compacted cylinders both in radial and axial directions. The behavior of green and recrystallized PTFE are supposed to be elastic. Using Young's modulus evolution with temperature obtained from a dynamic mechanical analysis (DMA) experiment, the stress can be computed inside the billet. Stress arises from the different of thermal expansion due to thermal gradients.

A Von Mises plastic behavior with low yield stress is added in the molten state. Therefore plastic strains form in the molten state resulting in residual stresses at end of the cooling. Residual stress maps can be computed as shown in Figure 1.22 .

This simulation has the advantage of carrying out a mechanical simulation of the PTFE billet sintering. The results are compared with residual stress measurements.

Prospective studies for improved PTFE sintering simulations

In order to be able to perform more accurate simulations of PTFE sintering, a better knowledge on the properties of green PTFE have to be acquired. Beside the behavior of molten PTFE was not studied.

Then a thermomechanical model for PTFE during sintering taking into account its viscoelastic, viscoplastic or elastoplastic behavior has to be defined. So far the existing

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

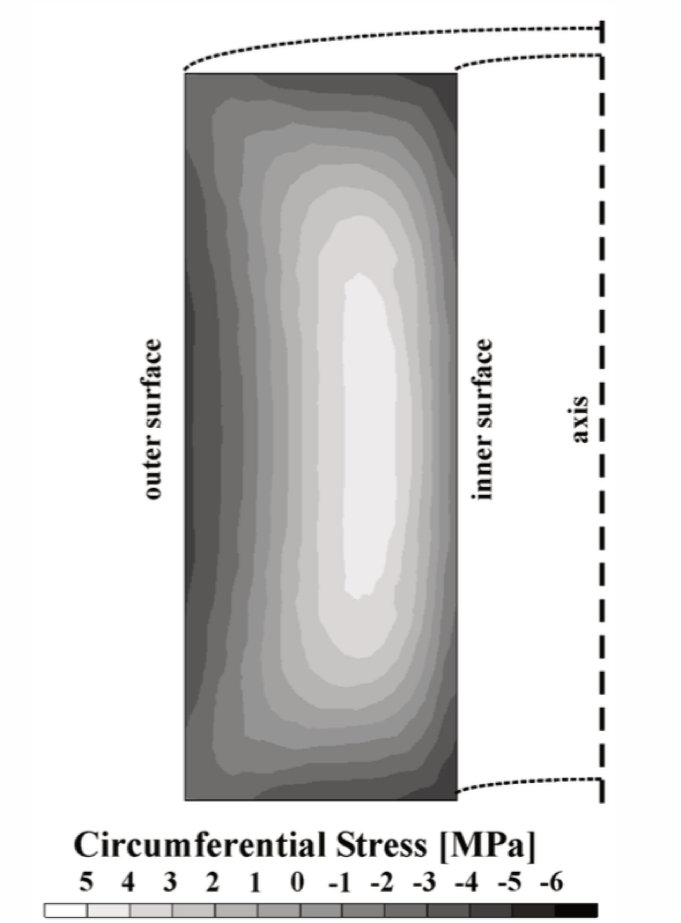


Figure 1.22: Circumferential residual stress map obtained from simulation of a billet sintering. Image taken from Andena [60].

models only reach 200°C.

The different thermal strain mechanism occurring during sintering could be modeled and especially to render the effect of crystallization kinetics.

Using those different models, a finer FE simulation could be developed. In particular, it could take into account variation of properties due to density gradients, and evaluate the effect of different crystallinity contents between core and edge. In Andena's simulation, the final residual stress is imposed by the plastic behavior of the molten state. As the whole billet has the same expansion coefficient, only the plastic strain can cause residual stresses in the end. This should be different when taking into account porosity closure and different crystallinity contents. It would also be interesting to investigate more on the properties of molten PTFE and get a precise mechanical model to improve the simulation.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Documents
Document Sharing Hub

Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Chapter 2

Material and methods

The material and the different experimental methods used to produce this PhD project are presented in this chapter.

Contents

1 Material 43
1.1 PTFE resin 43
1.2 Thermal characterization 43
1.3 Sample preparation: cold pressing and slicing 43
2 Differential scanning calorimetry (DSC) 46
2.1 Method description 46
2.2 Crystallinity evaluation from DSC† 46
2.3 Thermal gradient effects 47
3 Dilatometric measurements 48
3.1 Method description 48
3.2 Eigenstrain measurements† 49
3.3 Crystallinity content evaluation from dilatometry 50
4 X-Ray diffraction measurements (XRD)• 51
4.1 Method description• 51

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

4.2 Orientation measurement in transversely isotropic semi-crystalline polymers• 53
4.3 Experimental setups• 56
5 Microstructure observations 58
5.1 Microtomography 58
5.2 Scanning electron microscopy (SEM) 58
6 Thermo-mechanical testings 59
6.1 Dynamic mechanical thermal analysis (DMTA) 59
6.2 Compression tests in thermal chamber 60
6.3 Digital image correlation 62
6.4 Infrared thermography 63

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

Sections or subsections followed by an † are issued from the article:

PTFE crystallization mechanisms: Insight from calorimetric and dilatometric experiments, *to be submitted*

Sections or subsections followed by an • are issued from the article:

Orientation in transversely isotropic semi-crystalline polymer: application to uniaxially compacted PTFE, *to be submitted*

This chapter aims at presenting the material used in this study and the different experimental methods applied to characterized PTFE compacts behavior during sintering.

Section 1 deals with type of PTFE resin used and its pressing to form green parts. Differential scanning calorimetry (DSC) is presented in section 2. This technique is used to evaluate the thermal behavior, to characterize melting and crystallization in PTFE. In section 3, dilatometry is introduced to measure the thermal strain caused by a sintering cycle. An X-ray diffraction method for the characterization of the crystalline orientation in semi-crystalline polymers is described in section 4. Different observations methods detailed in section 5 were used to characterize and estimate the microstructure of PTFE compacts. Finally, the mechanical properties were evaluated thanks to different techniques and field measurement methods that are presented in section 6.

1 Material

1.1 PTFE resin

A fine cut (or low flow) granular PTFE resin was chosen. The initial crystallinity content of the powder is above 90 %. The molar mass of the powder is about 10^7 g/mol.

This type of resin is currently used for compaction molding and is suitable for compounding with fillers. More details on the difference between free flow, low flow resins and other type of PTFE powders are presented in Introduction .

On the SEM image of the PTFE powder in Figure 2.1, PTFE particles in the range of 20-100 µm can be observed. Those particles appear as fluffy flakes with a complex sub-microstructure (Figure 2.1b). The individual size of those elements is in the range of 100-500 nm. Therefore, two types of porosities can exist in the material after compaction, one *macro-porosity* to be linked with the particles size itself and a *micro-porosity* at a submicrometric scale. Chapter 4 deals with porosity and their evolution during sintering.

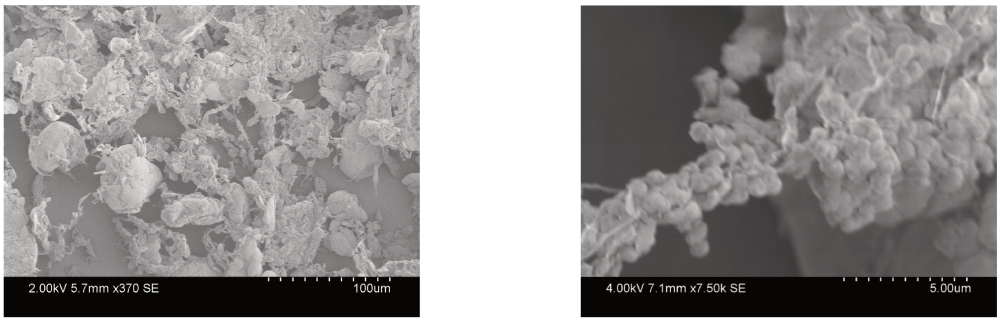
1.2 Thermal characterization

A calorigram of compacted PTFE is shown Figure 2.2. This experiment was performed on a differential scanning calorimeter with a 5 mg sample heated up at 20°C/min. The calorigram shows that the melting temperature of this resin is close to 340°C. It highlights an inflexion close to 250°C revealing a diffuse phase transition below the melting peak that could correspond to the melting of smaller crystals.

1.3 Sample preparation: cold pressing and slicing

In this work, PTFE compacts obtained (mostly) from uniaxial compaction are studied. Uniaxial pressing consists in filling a rigid die with PTFE powder and then compacting it by applying pressure with a piston. Figure 2.3 illustrates the powder compaction.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles



(a) (b)

Figure 2.1: SEM observation of the PTFE powder used for the experiments. (b) is a zoom of (a). The images are coming from an earlier work [10].

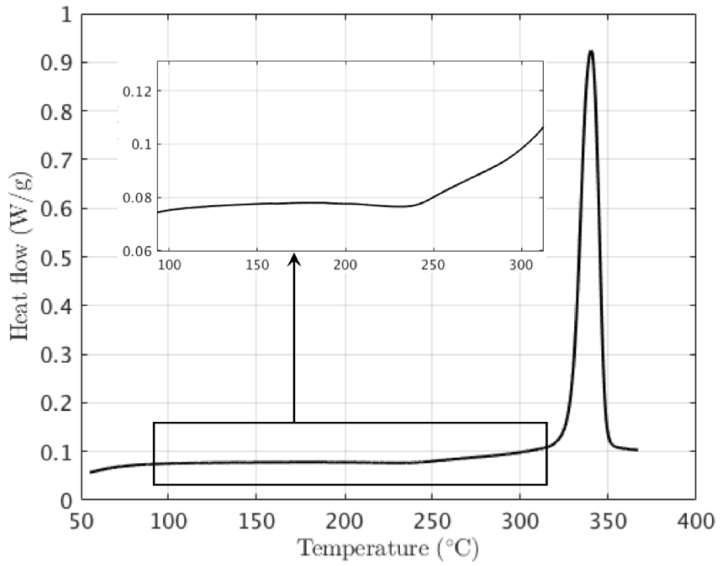


Figure 2.2: DSC melting peak of compacted PTFE powder. A zoom is shown at lower temperatures where a change is observed around 250°C

For all the experimental methods described in this chapter, the die of cross-section 8 mm × 8 mm was used to shape either cubes or rectangular blocks depending on the quantity of PTFE placed in the die. Density gradients and skin effects are induced by uniaxial compaction. The former is reduced by having a height as small as possible. The latter is considered to have little effect on dilatometry and is therefore neglected.

Another square die of section 35 mm × 35 mm was used to make 2 mm thick plates for the simulation validation experiment described later. A circular cross-section die with a diameter of 30 mm was used to make 20 mm high cylinders for another type of validation experiments (see Chapter 8).

The compaction was made on universal testing machine with an actuator displacement speed of 1 mm/min up to a given pressure. Then the actuator displacement was fixed for 5 min before unloading. The compaction pressure was mostly set at 50 MPa but samples were compacted at lower pressures to investigate the influence of the specimen green density

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

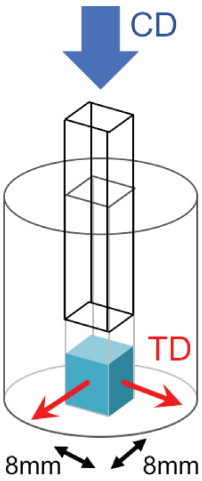


Figure 2.3: Uniaxial compaction of PTFE powder inside a metal die of 8 mm square section. The compaction direction (CD) and transverse directions (TD) are indicated.

on its dilatometric behavior during sintering in Chapter 4.

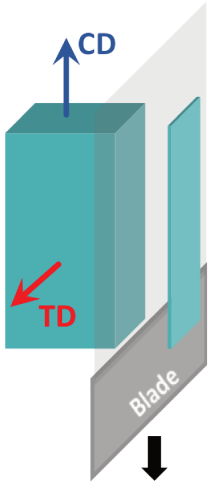


Figure 2.4: PTFE compacts are cut using a microtome to obtain 100 and 300 µm thick slices.

For differential scanning calorimetry (DSC) and for X-ray diffraction experiments (XRD), the PTFE blocks were sliced using a microtome (see sketch in Figure 2.4). 100 and 300 µm thick slices were obtained. The skin was always removed from the uniaxially pressed sample to measure only properties at the core. The cut were performed at ambient temperature. A preliminary cooling of the sample with liquid nitrogen could have been done to avoid any reorientation effects due to slicing. However no significant effect was noticed from the cut, so the cooling was not tested.

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

2 Differential scanning calorimetry (DSC)

2.1 Method description

Differential scanning calorimetry (DSC) is a thermal analysis method. It measures the heat energy uptake for a specific a thermal history. This method is used to characterize phase transitions. From the heat flow measurement, the transition temperature and the enthalpy associated can be estimated. For semi-crystalline polymers, this method is widely used to determine the glass transition, melting and crystallization [74, 75]. DSC is very convenient to study crystallization kinetic [76, 77].

The DSC method consists in measuring the temperature of the sample and of a reference sample, both placed in a precisely controlled oven. The temperature difference between the sample and the reference is related to the energy released or absorbed by the sample. At constant cooling or heating, it is linked to the specific heat capacity and latent heat of a phase change (see subsection 2.2).

To perform DSC on PTFE compacts, PTFE slices were punched into 5 mg disks. The thickness of the sample was limited to 100 µm to reduce thermal gradients (see subsection 2.3. The disk was placed in an standard aluminum pan (20 mg). A TA instruments Q10 was used for the DSC experiments. The heating and cooling rates were set between 0.5 to 20°C/min.

2.2 Crystallinity evaluation from DSC†

The specific heat of each phase, amorphous and crystalline, resp. $c_p^{\text{am}}(T)$ and $c_p^{\text{cr}}(T)$, can be well described as an affine variation with temperature. However the overall specific heat $\widetilde{c_p}$ is not linear with temperature during the crystallization as it depends on the crystalline mass fraction χ

$$\widetilde{c_p}(T,\chi) = \chi c_p^{\text{cr}}(T) + (1-\chi)c_p^{\text{am}}(T) \tag{2.1}$$

As the crystallinity content χ obeys a specific kinetic, it is not only dependent on temperature but also on thermal history, or during the DSC measurement performed at constant cooling rate, $\dot{T} = \phi$, on time and hence so does $\widetilde{c_p}$.

Ideally, the specific heat flux $\dot{q}$ extracted from a sample subject to melting or crystallization in a DSC experiment obeys

$$\dot{q} = \widetilde{c_p}\dot{T} + \Delta h^{\text{am-cr}}\dot{\chi} \tag{2.2}$$

where $\Delta h^{\text{am-cr}}$ is the specific heat of crystallization.

It is to be noted that both equations (2.1) and (2.2) are non-linearly coupled, so that the evaluation of χ during a DSC measurement at fixed cooling rate, $\dot{T} = \phi$, cannot be directly obtained. It is proposed to estimate χ from an iterative process where the above equations are progressively made consistent with each other at convergence through a fixed-point algorithm.

To evaluate the crystallinity content as a function of time (or temperature using the prescribed (constant) cooling rate $\dot{T} = \phi$), a baseline heat flux only due to the temperature change at fixed phase mass fraction, $\dot{q}_{\text{base}}(t) = \widetilde{c_p}\dot{T}$, is introduced. However the measurement of c_p^{cr} for purely crystalline is not directly available for the computation of $\widetilde{c_p}$, so the asymptotic baseline of the recrystallized state $\dot{q}_{\text{base}}^{\text{recr}}(t)$ is used instead.

$$\dot{q}_{\text{base}}(t) = \frac{\chi(t)}{\chi^\infty}\,\dot{q}_{\text{base}}^{\text{recr}}(t) + \left(1 - \frac{\chi(t)}{\chi^\infty}\right)\dot{q}_{\text{base}}^{\text{am}}(t) \tag{2.3}$$

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

where χ^{∞} is the estimated asymptotic crystallinity at room temperature evaluation of the recrystallized PTFE. $\dot{q}^{\text{recr}}_{\text{base}}(t)$ is related to $\widetilde{c_p}(T, \chi^{\infty})$ at the end of the crystallization which is dependent on $\dot{T} = \phi$.

The integration of $\dot{q}_{\text{exp}}(t)$ from which the baseline $\dot{q}_{\text{base}}(t)$ has been subtracted gives an evaluation of the crystallinity content $\chi(t)$ for a given cooling rate ϕ

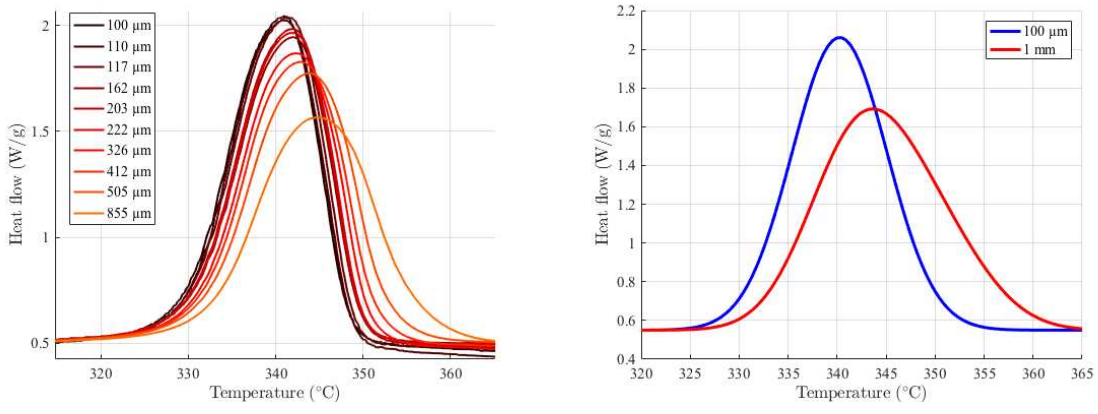
$$\chi(t) = \frac{1}{\Delta h_{\text{am-cr}}} \int_{t_0}^{t} \left(\dot{q}_{\text{exp}}(t') - \dot{q}_{\text{base}}(t') \right) \mathrm{d}t' \tag{2.4}$$

where t_0 is the time of crystallization onset.

To initiate the determination of $\chi(t)$, a first evaluation is performed from the calorigram using a linear baseline for integration. Then, a new baseline is computed from Eq. (2.3), and from the latter, $\chi(t)$ is time integrated using Eq. (2.4). These two steps are repeated up to convergence to a fixed point, which requires typically no more than 2 to 3 iterations. This computation is performed in Chapter 5. Figure 5.2 shows the crystallization peak, the baseline at convergence and the integrated area.

2.3 Thermal gradient effects

In DSC experiments as the heating/cooling rates be significant compare to the sample thickness, thermal gradients can considerably modify the measurement. To gauge this effect, DSC experiments were performed on green PTFE at melting for various thicknesses at 20°C/min. The samples of different thicknesses were obtained by stacking PTFE disks in the DSC pan and therefore increasing the sample mass. Figure 2.5a shows the DSC signal for samples with different thicknesses. The melting peak widens due to thermal gradient as the thickness of the sample increases. Thermal gradients delay the heating in the core region causing a widening of the peak. This thermal delays effect on the melting peak can be retrieved by a mere thermal simulation. Figure 2.5b shows the melting peak simulated for a 100 µm and a 1 mm thick samples.



(a) (b)

Figure 2.5: DSC melting curves obtained for samples with different thicknesses at 20°C/min (a). A widening and a shift of the melting peak is observed for thicker samples. The same effect is retrieved with a thermal simulation of the DSC melting curve for 100 µm and 1 mm thick samples (b).

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

The same effect can be observed if the heating rate is too important. From the thermal simulation a sample heated up at 20°C/min the thermal gradient did not affect significantly the melting peak shape. Above 50°C/min thermal gradients are likely to modify the results for a 100 µm thick sample.

Therefore, one must be very careful when analyzing DSC results to be sure no thermal gradient effects are to be taken into account. At least, results should be compare in the same conditions (same thickness and heating/cooling rates). Studying crystallization kinetics requires to vary the cooling rates and thus the thermal gradient has to be carefully handle. It is important to choose sample thin enough and cooling rates not to high. Thus, the PTFE samples thickness was set at 100 µm and the heating/cooling rates did not exceed 20°C/min.

3 Dilatometric measurements

3.1 Method description

Dilatometry is a thermal analysis technique consisting in measuring the length or the volume evolution of a sample with temperature. Thermomechanical analysis (TMA) is the dilatometry method where the sample is maintained under a slight tension or compression during the thermal cycle. In practice, dilatometry is performed in a thermomechanical analyzer with load as small as possible to only ensure contact during measurement. Dilatometry is used to access thermal expansion coefficients and to study phase transitions.

For PTFE compacts, this experiment is able to reproduce sintering cycles at a small scale with quite uniform temperature in the specimen. During the sintering cycles, small PTFE cubes are melted and then recrystallized. The dilatometric measurements can also be compared to DSC measurements as they both give information on phase changes; here melting and crystallization (see Chapter 5).

For this work, PTFE cubic specimens were placed inside a thermomechanical analyzer TMA/SDTA 840 from Mettler Toledo. The oven controls the temperature and a probe placed on top of the sample measures its dimension (see Figure 2.6). The force applied by the probe was imposed at 0.01 N.

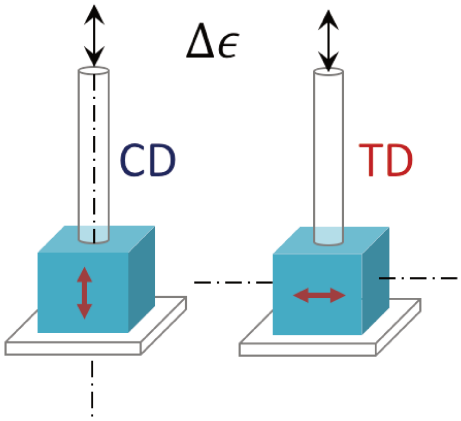


Figure 2.6: Measurement of the sample dimension variation during a thermal cycle in the compaction direction (CD) and in the transverse direction (TD).

Note that the dilatometric experiments on PTFE compacts were very repeatable inso-

AVA Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles

far as the preparation conditions were the same. Dilatometric results appear to be sensitive to the compaction conditions. In particular, the powder temperature and maybe the hygrometry seem to modify the dilatometric behavior. To maintain the reproducibility of the experiments, the powder was stored at 4°C in a refrigerator before to compaction to remain below the crystalline phase transition at 19°C

Assuming a homogeneous state (from quasi-static temperature variations) the true (or logarithmic) strain ε_{ii} in direction i = CD *or* TD can be estimated from the displacement u_i and the initial size L_i, as

$$\varepsilon_{ii} \equiv \log\left(1 + \frac{u_i}{L_i}\right) \tag{2.5}$$

all along the thermal cycle (no implicit summation on index i). Note that this is the *mean* strain from the initial state considered as a reference, and the current state. Resorting to true strains allows us to change reference if so desired by mere subtraction of the strain of the newly chosen reference state.

The dilatometry test is performed on different samples, some to test the compaction direction (CD) and others for the transverse direction (TD) as the samples are transversely isotropic due to the uniaxial compaction (Figure 2.3).

From this transverse isotropy symmetry, the strain tensor is expected to be fully characterized by the TD and CD strain components. Choosing the third axis along the CD, the strain tensor assumes the following form

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{TD} & 0 & 0 \\ 0 & \varepsilon_{TD} & 0 \\ 0 & 0 & \varepsilon_{CD} \end{pmatrix} \tag{2.6}$$

3.2 Eigenstrain measurements†

In the dilatometric experiments, the temperature gradient was limited to a few degrees Celsius by choosing heating and cooling rates of maximum 2°C/min. Thermal computations showed that at this heating rate, the thermal gradient is maintained to 2°C between core and the edge of the specimen. Because of the homogeneity assumption and the assumption that the applied force is null, the measured strains are actually "eigenstrains" for constitutive law formulation of the thermo-mechanical behavior.

Eigenstrains correspond to the strains not related to external forces [78]. Among those stress-free strains are the thermal expansion and strain related to phase transformation. In practice, the eigenstrain is defined at the scale of the representative volume element (RVE). During phase transformations part of the microstructure can be constrained even if the stress is null at the scale of the RVE. The overall eigenstrain gathering the different eigenstrain components is expressed as ε^*_{ii}.

From the previous assumptions, the measured strains for PTFE compacts will be considered equal to the overall eigenstrain of PTFE,

$$\varepsilon_{ii} = \varepsilon^*_{ii} \tag{2.7}$$

During sintering, the eigenstrain of PTFE is caused by various physical mechanisms such as thermal dilation, phase change, void closure and residual stress relaxation. Those mechanisms will be studied in the next chapters (Chapters 3,4 and 5).

Documents
Document Sharing Hub
Full document details: Frittage de pièces de Polytétrafluoroéthylène (PTFE) compacté : Mécanismes physiques et modèles