Universitat de Girona

CONTRIBUTION TO ULTRASONIC MICRO-MOULDING PROCESS OF HIGH PERFORMANCE POLYMERS

Tomasz Dorf

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DOCTORAL THESIS

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2019

DOCTORAL PROGRAMME IN TECHNOLOGY

Supervised by: Joaquim de Ciurana Gay
Tutor: Joaquim de Ciurana Gay

Presented in partial fulfilment of the requirements for a doctoral degree from the University of Girona

Dr Joaquim de Ciurana, of Department of Mechanical Engineering and Civil Construction, University of Girona

I DECLARE:

That the thesis titles "*Contribution to micro-moulding process of high performance polymers*", presented by Tomasz Dorf to obtain a doctoral degree has been completed under my supervision.

For all intents and purposes, I hereby sign this document.

Signature

Girona, 02.10.2018

To my daughter Milenka.

Acknowledgements

List of publications

This doctoral thesis is presented as a compendium of publications. The following list contains the publications presented as chapters of this PhD.

CHAPTER 3: Dorf, T., Perkowska, K., Janiszewska, M., Ferrer, I., Ciurana, J. (2018). Effect of the main process parameters on the mechanical strength of polyphenylosulfone (PPSU) in ultrasonic micro-moulding process. Ultrasonics – Sonochemistry, 46, 46-58.

For 2017, the journal ULTRASONICS-SONOCHEMISTRY has an Impact Factor of 6.012.

CHAPTER 4: Dorf, T., Ferrer, I., Ciurana, J. (2018). The effect of weld line on tensile strength of polyphenylosulfone (PPSU) in ultrasonic micro-moulding process. Submitted in The International Journal of Advanced Manufacturing Technology (in revision).

For 2017, the journal INTERNATIONAL JOURNAL OF ADVANCED MANUFACTURING TECHNOLOGY has an Impact Factor of 2.601

CHAPTER 5: Dorf, T., Ferrer, I., Ciurana, J. (2018). Characterizing ultrasonic micro-moulding process of polyetheretherketone (PEEK). International Polymer Processing, 33, 442-452.

For 2017, the journal INTERNATIONAL POLYMER PROCESSING has an Impact Factor of 0.535.

List of acronyms

µICM	Conventional micro-injection mould
µIM	Micro injection moulding
µVIM	Ultrasonic vibration micro-injection mould
ANOVA	Analysis of variance
HPPs	High performance polymers
MEMS	Micro-Electrical Mechanical Systems
micro-UPM	Micro-ultrasonic power moulding
PMMA	Polymethyl methacrylate
PA 12	Polyamide 12
PEEK	Polyetheretherketone
PLA	Polylactide
PPSU	Polyphenylsulfone
PP	Polypropylene
PS	Polystyrene
PS/HDPE	Polystyrene/high-density polyethylene
SEM	Scanning Electron Microscope
TGA	Thermogravimetric analysis
UHMWPE	Ultra-high-molecular-weight polyethylene
UAIM	Ultrasonic assisted injection moulding
UIM	Ultrasonic injection moulding

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Els materials polimèrics de altes prestacions són considerats apropiats per desenvolupar diferents aplicacions, en especial en el cas dels implants o próstesis mediques. El procés de injecció o en el seu defecte la micro-injecció ve essent utilitzada per la fabricació en grans volums, però resulta inapropiat per la fabricació de petites sèries pel seu cost econòmic.

Recentment els avanços realitzats en la tecnología del moldeig per ultrasons ha fet que aquesta sigui una tecnología més apropiada per la fabrició de petites sèries. El moldeig per ultrasons permet fondre, moldejar i solidificar la quantitat necessària per fer una peça petita, evitant així una gran pèrdua de material en les zones de colades. Aquesta tesi doctoral és una contribució al coneixement del procés de micro-injecció per ultrasons amb materials d'altres prestacions com el polifenilsulfona PPSU i el polietereetercetona PEEK, establint relacions entre els paràmetres de processat i les propietats mecàniques del producte, establint un aspecte clau en la producció de futures peces.

Los materiales poliméricos de altas prestaciones son considerados apropiados para desarrollar diferentes aplicaciones, en especial en el caso de los implantes o próstesis médicas. El proceso de inyección o en su defecto la micro-inyección viene siendo utilizada para la fabricación en grandes volúmenes, pero resulta inapropiado para la fabricación de pequeñas series por su coste económico.

Recientemente los avances realizados en la tecnología del moldeo por ultrasonidos ha hecho que esta sea una tecnología más apropiada para la Fabricio de pequeñas series. El moldeo por ultrasonidos permite fundir, moldear y solidificar la cantidad necesaria para hacer una pieza pequeña, evitando así una gran pérdida de material en las zonas de coladas. Esta tesis doctoral es una contribución al conocimiento del proceso de micro-inyección por ultrasonidos con materiales de altas prestaciones como el PPSU y el PEEK, estableciendo relaciones entre los parámetros de procesado y las propiedades mecánicas de la pieza, estableciendo un aspecto clave en la producción de futuras piezas.

Polymeric materials, which are suitable for high performance applications for example human implants are one of the most expensive available polymers. Standard injection micro-moulding process, dedicated for mass production, it is often uneconomical for low-series or single-piece production.

Recently available ultrasonic-micro moulding technology, which can plasticize only amount of polymers required for one part seems to be a potential alternative to standard injection micro-moulding technology especially by limiting the waste of materials during small production runs. This thesis focus on increasing knowledge about the ultrasonic micro-moulding process of polymers, such as polyphenylsulfone PPSU and polyetheretherketone PEEK, establishing relationship between the process parameters and the key aspect of the high performance parts such as mechanical properties.

Materiały polimerowe odpowiednie do zastosowań w wymagających aplikacjach, takich jak implanty medyczne, są jednymi z najdroższych dostępnych polimerów. Standardowy proces wtryskiwania, który jest dedykowany do masowej produkcji, okazuje się nieekonomiczny dla małych oraz krótkich serii produkcyjnych.

Ostatnio dostępna technologia wtryskiwania ultradźwiękowego, która jest w stanie roztopić oraz wtrysnąć ilość materiału niezbędną dla jednego cyklu, może być alternatywą dla standardowych procesów wtryskiwania, szczególnie jeśli chodzi o zmniejszenie strat materiałowych podczas małych serii produkcyjnych. Ta rozprawa doktorska skupia się na rozszerzeniu wiedzy odnośnie technologii wtryskiwania ultradźwiękowego polimerów, jak polifenylosulfon (PPSU) oraz polieteroeteroketon (PEEK), ustalając związek pomiędzy parametrami procesu a kluczową właściwością wyrobów z tworzyw wysokotemperaturowych, jaką jest wytrzymałość mechaniczna.

Chapter 1. Introduction

Chapter 1 presents the general introduction of the ultrasonic micro-moulding technology and it introduces the interest of the work and it determines the motivation for this thesis.

1.1. Ultrasonic micro-moulding technology

Ultrasonic micro-moulding technology utilize the vibration energy as a source to melt the polymeric material. The technology is capable to manufacture micro parts characterized by the properties similar to those obtained from the conventional micro-injection moulding technology. The first commercial ultrasonic moulding machine was launched on the market in 2013 by Ultrasion S.L. Since then, Sonorus 1G machine has been constantly developed and improved. Apart from commercial and industry applications, ultrasonic micro-moulding technology are in interest of scientist, who focus on the understanding the process and investigation how processing parameters influence on the physical and chemical characteristic of materials.

Ultrasonic micro-moulding approaches the manufacture of the micro parts from different perspective. The material are plasticized using ultrasound so there are no need to use heaters and in consequence there is no material residence time, which could lead to thermal degradation of the polymer. In addition, as the energy needed in the process, it is only at the point when the ultrasonic horn contacts the raw material to induce melt, it uses upwards of 90 percent less energy than a traditional micro-injection technology. Moreover, in the process, material is dosing in the amount necessary only for one cycle directly to the mould, thus the huge material savings can be observed (Fig. 1.1). Polymers melted exhibit reduced viscosity, what allows production of thinner walled parts contrary to standard technology. High intensity

mechanical vibration transmits energy directly into the polymer molecular structure causing very fast melting in whole volume of granule. The reduced viscosity means that the process uses lower moulding pressures of 300-400 bar than alternative micro-moulding technologies using usual pressure of 1500-2000 bar. Applications, which production enforces the use of moulds with a small diameter core pins can be moulding without risk of damage.

Fig 1.1. Ultrasonic micro-moulding machine (courtesy of Ultrasion S.L.)

All this features indicate, that the ultrasound technology can be considered as a manufacturing alternative mainly for sensitive and expensive polymers. Table 1.1 shows basic differences between two technologies (Surace et al., 2012, www.ultrasion.com).

Table 1. 1. Technologies differences

Features	Technology	
	Micro-injection moulding	**Ultrasonic micro-moulding**
Energy type	Calorific (internal molecular vibration)	Kinetic + Calorific
Source of heat energy	Screw and heaters	Ultrasounds

Adjustable main process parameters	Melt temperature, Injection speed, Injection pressure, Holding pressure, Holding Time, Cooling time, Mould temperature	Amplitude, Plunger Velocity, Ultrasonic time, Cooling time, Mould temperature
Residual time	Yes	No
Moulding pressure	High	Low
Material usage	necessary for fulfil the barrel	only for one cycle
Mould	complicate	simple
Melted material viscosity	Higher	Lower
Energy consumptions	High	Low
Available knowledge of the process	High	Low

1.2. Interest

This Thesis is carried out as a result of cooperation between a medical company ChM sp. z o.o. (producer of implants and instruments for orthopaedic and traumatology) in which the author works and Ultrasion S.L., a company that commercialized the ultrasound technology. The aim of cooperation is the development of ultrasonic micro-moulding process for the processing of new polymeric materials occurring in medical sector.

The global medical polymers market size was estimated at USD 12.34 billion in 2016 and is constantly growing. The increase in average age of population lead to increase of healthcare treatment. Medical polymers are utilizes in variety applications like devices, packaging and others such as tissue engineering, cardio implants, etc. (Grand View Research, 2017).

Working on new medical implantable products, while selecting polymeric materials not only physical, chemical and biological properties should be considered but also regulatory concerns related to the material. To be accepted as biomaterial a new material's biocompatibility must be evaluated by in vivo animal experiment (Yaszemski and Trantolo, 2004). Requirements, such as purity, biocompatibility, resistance for sterilization and compliance with all medical directives cause a very high price for this type of polymers. For example, biomaterials, such as biodegradable PLA (Modjarrad and Ebnesajjad, 2014) or representative of high performance polymers polyetheretherketone (PEEK) (Kurtz and Devine, 2007) - their cost oscillate between 2.000 and 3.000 EUR per kilo depending on the type.

Considering diverse and low-volume implants production from such expensive materials in the context of using standard injection micro-moulding technology, the process seems to be uneconomic. There are several factors by which such as a conclusion was made:

- the material waste needed to start and finish the injection process;
- the material waste on the sprue compared to the micro-product itself;
- high costs of injection moulds;
- the risk of material degradation due to the residence time of polymer,
- maintain the cleanness of the injection unit between productions.

All these factors influenced the decision to focus on research and acquire the knowledge about ultrasonic micro-moulding process as a solution for limitations of the injection micro-moulding process.

1.3. Motivation

Technologies available to manufacture polymeric parts are designed and dedicate to mass production. Machine manufacturers tend to focus on continuously increasing production efficiency by lowering cycle time and makes the process cheaper. This is an understandable approach from the point of view of short or single use of the product.

In medical sector in terms of low-series production from high performance polymers such as polyphenylsulfone (PPSU) and polyetheretherketone (PEEK), high production efficiency goes to the background. Here, the factor such as savings material is of the greatest importance. Therefore, gaining knowledge on the processing of high-temperature polymers in ultrasonic technology will allow to significantly reduce production costs, which in turn will also affect the price of the final product making it more achievable for the patients.

The following lists of advantages and disadvantages can show the different aspects related to ultrasonic micro-moulding technology (Table 1.2).

Table 1. 2. Advantages and disadvantages

+	-
- Energy savings of the machine. - Material savings during the process. - Reduced moulding pressure. - Reduced viscosity in melted material. - No residence time. - High precision. - Knowledge regarding processing of commodity and engineering polymers.	- Limited knowledge regarding process compare to the conventional injection micro-moulding technology. - Experimental and scientific lack of knowledge regarding process of high performance polymers. - Lack of knowledge regarding weld line formation of the parts in the ultrasonic process. - The machine is not adapted to processing of high performance polymers.

Overcoming the limitation in ultrasonic micro-moulding technology listed above, it can be made the following initial hypothesis:

"Employing the up-to-date knowledge of ultrasonic micro-moulding process it is possible to process high temperature and expensive polymers such as PPSU and PEEK obtaining not degraded parts with mechanical strength comparable to the products from conventional injection-micro moulding technology".

To achieve it, it is necessary to work on the following issues:
- Modify the mould so that capable to maintain the temperature in the range of 140-180° C.
- Improve the ultrasonic micro-moulding process as suitable to manufacturing parts from PPSU and PEEK polymers.
- Improve the knowledge related to ultrasonic process parameters and their influenced on the mechanical strength.

1.4. Objectives

The main objective of the thesis is to extend existing knowledge in the ultrasonic micro-moulding process, defining the parameters involved and analysis their influence on the tensile strength and degradation of the parts.

This thesis aims to develop studies and experiments needed to reach a level of knowledge of the process parameters and their dependents in order to successful utilize ultrasonic micro-

moulding technology for manufacturing the parts from PPSU and PEEK polymers. Moreover, the investigation of weld line formation using this novel technology was performed.

The objectives of the thesis can be divided into more specifically:

- Analyse the combination of the main ultrasonic micro-moulding parameters on the mechanical properties and chemical characteristic of PPSU.

- Investigation the morphology of the surface in the PPSU samples.

- Develop the model for selecting the appropriate values for the input process parameters when using ultrasonic micro-moulding technology to produce PPSU parts characterised by their high mechanical strength.

- Focus on the weld line formation and its influence on tensile strength in PPSU parts fabricated from ultrasonic micro-moulding process.

- Analyse the process parameters influence when processing the PEEK polymers using ultrasonic vibration due to obtain parts with competitive properties to the parts from conventional micro-injection moulding technology.

Achieving the objectives will allow to improve the knowledge in order to extend the processing capabilities of ultrasonic micro-moulding technology of high requirement polymers such as PPSU and PEEK.

1.5. Thesis structure

The Thesis consists of the following chapters:

Chapter 1 presents short introduction of the ultrasonic micro-moulding technology, interest, motivation and objectives of this work.

Chapter 2 reviews the state of the art related to the manufacturing polymeric micro parts, developments of injection moulding technology and introduce research regarding ultrasonic micro-moulding process.

Chapter 3 presents the investigations of the main ultrasonic micro-moulding parameters on the mechanical properties and chemical characteristic of parts made from PPSU polymer.

Chapter 4 focus on the weld line formation issue and its influence on the tensile strength of the PPSU parts in ultrasonic micro-moulding technology.

Chapter 5 characterize the ultrasonic micro-moulding process of PEEK polymer.

Chapter 6 summarizes results and discussion.

Chapter 7 presents conclusion and outlook. The list of publications is presented at the end of this chapter.

Figure 1.2 shows the relationships between the different chapters of the thesis.
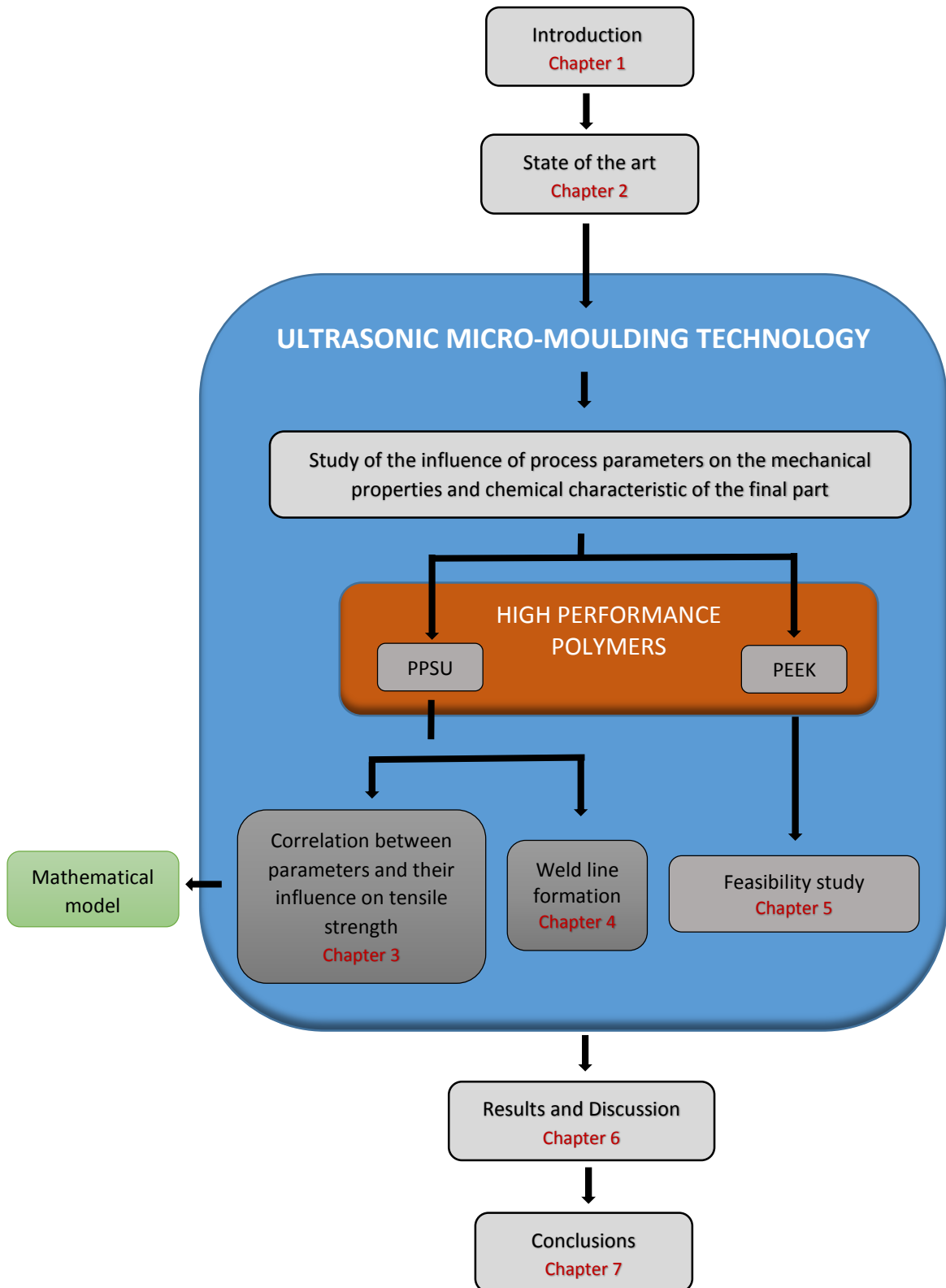
Fig. 1.2. Structure of the Thesis.

Chapter 2. State of the art

Chapter 2 reviews state of the art of micro injection moulding process and the technology development to meet the requirements for production of polymeric micro parts. Afterwards, introduce the ultrasonic micro-moulding technology and present research and scientific work on this novel manufacturing process. Finally, polymers such as PPSU and PEEK in the context of their properties and applications are described.

2.1. Introduction

The miniaturization, which has been progressing for years is present in nearly every industry. In electronics Micro-Electrical Mechanical Systems (MEMS), an extremely small mechanical or electro-mechanical systems, have spurred major advancement. MEMS can be utilized for a wide variety of applications in almost every industry. Another great beneficiary of miniaturization is communication. For example, current available cell phones have enough functionality to provide multiple communication platforms, entertainment, internet access, and so on, and are much smaller than firstly available phones with the function of make calls only. Like the former industries also the medical and automotive have embarked on a radical transformation. The need for more and more new micro elements made of polymeric materials, such as microfluidic devices forced the development and improving current micro moulding technologies (Attia et al., 2009).

Micro polymeric component can be defined as the part with the mass in milligrams, which exhibits dimensions with tolerances in the micrometric range (Surace et al., 2012). To meet rising requirements of micro polymeric parts not only the conventional injection micro

moulding technology has been developed but also new approaches to moulding micro components has been introduced.

2.2. Micro-injection moulding technology

Micro injection moulding (µIM) is one of the most efficient and common process for the large scale production of polymeric materials. The process was developed in the late 1980s with modified conventional injection moulding machines (Piotter et al., 2001, 2002). In conventional moulding machines polymer is plasticized from a thermal and mechanical heating supplied by a screw in a barrel. The weight of the parts represents only a few percentage of the whole shot weight what lead to a large amount of material wastes. Additional small dozes contribute to long residence time and finally to degradation of the polymer left in a barrel. Also small clamp forces are required because of the small surface of injected polymers. Therefore, the size of the injection unit (screw, barrel, nozzle) and the clamp unit can be decreased to lower the amount of material and energy consuming (Giboz et al., 2007). Currently commercial micro moulding systems units for conventional machines are produced, inter alia, by Ferromatic Milacron, Arburg and Sumito Demag, whilst Wittmann-Battenfeld, Babyplast and Desma offers dedicated micro injection moulding machines.

In parallel to development of µIM by leading companies, the topic of improving the process also found interest in scientists. There have been several works of development the process to overcome the limitation of the standard injection micro-moulding process.

2.2.1. Micro-injection moulding process development

Chang et al. (Chang et al., 2007) developed an external-type microinjection moulding module for thermoplastic polymer (Fig. 2.1). The designed system could be applied on small tonnes reciprocating screw hydraulic or fully electric injection moulding machines and the shape of module is like a part of mould combined with servomotor and transmission mechanism.
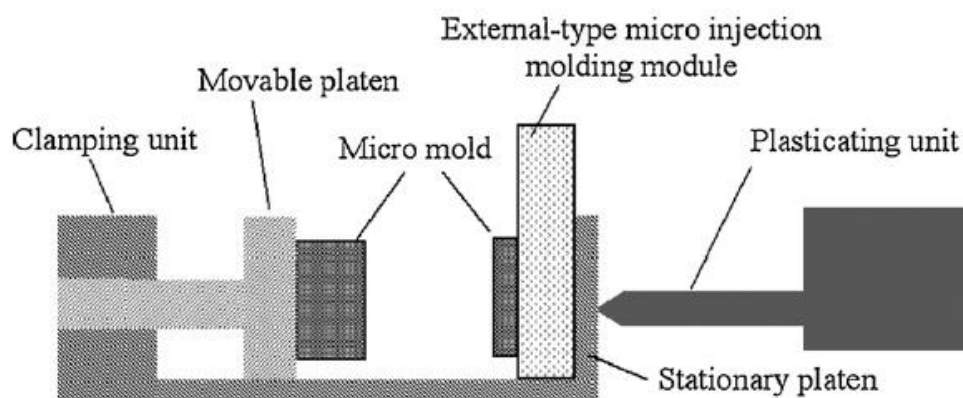
Fig. 2. 1. Schematic of the external-type micro-injection moulding module (Chang et al., 2007).

The main characteristics of the concept were:
- The module could be applied to most reciprocating injection moulding machine.
- High precision of metering and injection the resin is provided by the plunger instead of reciprocating screw.
- A special hot runner is used as the metering barrel and a pin valve is selected to control the open-close of the injection nozzle.
- A servomotor and a ball screw are used to accomplish accurate metering and high injection speed.

From the moulding experiments, an external micro injection moulding module indicated the performance at least of the same level as the two-stage screw-plunger injection moulding machine. Moreover, the module is even better for ultra-small metering volume case.

Oyetunji (Oyetunji, 2010) worked on the prototype for producing small plastic articles in small-scale production. His injection machine made from mild steel and medium carbon steel consist of two basic elements, the injection unit and the clamping unit (Fig. 2.2). The aim of the research was to design, construct and testing of small injection moulding machine.
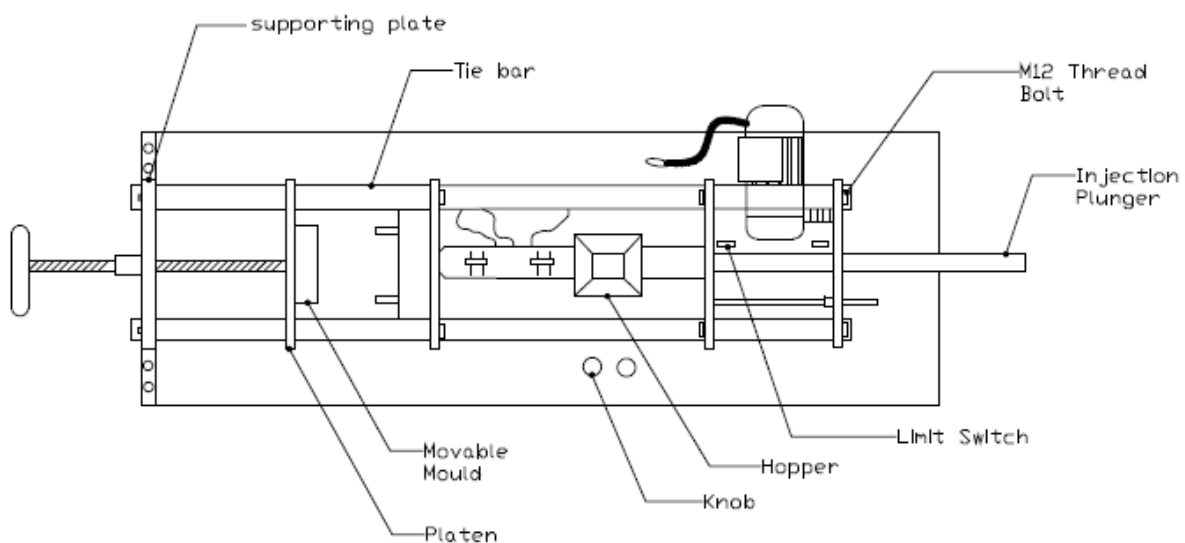
Fig. 2. 2. Plan view of the injection moulding machine (Oyetunji, 2010).

However the design, construction and testing had been successfully accomplished, it was found some problems in the moulding process such as:
- Moulding was not fully injected.
- Sinks or blisters were appeared on the product or moulding.
- Product discolours was observed.

Later on, Bloß et al. (Bloß et al., 2014) proposed and designed a two-step plunger system shown in Figure 2.3 to fulfil the requirements for managing small shot volumes with high reproducible and accuracy what influence on decreasing the residence time.
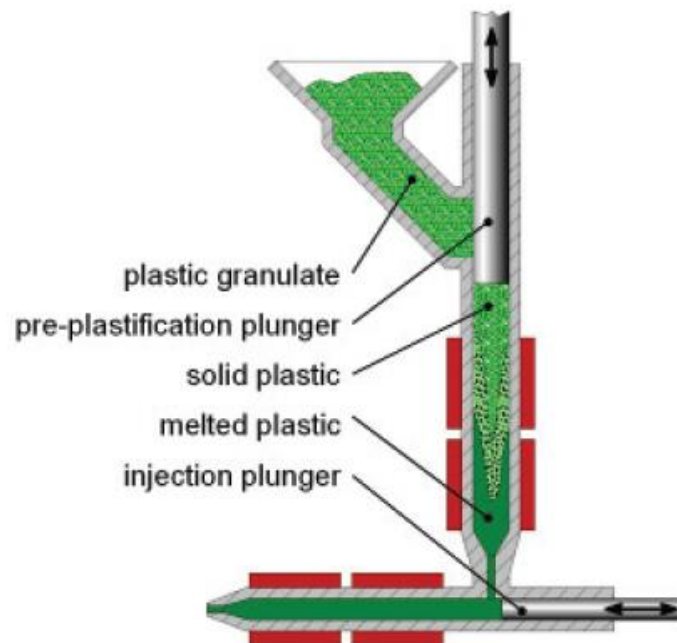
Fig. 2. 3. Scheme of the two-step plunger system (Bloß et al., 2014).

The melt is pressed through a thin hole into the heated barrel. The diameter of the injection plunger is between 2 and 3mm. Optimized two-step plunger injection units permit processing at very short residence times and a high volume resolution for cavity filling. It is applicable both to small series and mass production with high efficiency concerning material economy, cycle time and mould costs.

2.2.2. Ultrasonic assisted injection moulding process

Apart from challenges with metering and residence time during the micro-injection moulding process, another important issue including filling process and replication were investigated by the researchers as well.

Lee et al. (Lee and Kim, 2008) analysed numerically the effects of ultrasounds vibration in filling process during injection moulding. They showed that the ultrasonic vibration has strong effect on filling phase with various velocity fields of each modes. By increasing magnitude of velocity field, it is possible to improve the filling rate of polymers melt. Furthermore, ultrasonic vibration lowers the viscosity and influence on filling time. This may help to solve the cooling problem of polymer melt due to filling process in a short time.

According to Sato et al. (Sato et al., 2009) ultrasonic vibration lead to improved replication properties and decreased the residual strain of injection moulded part. The investigations were carried out using developed ultrasonic injection moulding (UIM), which applied ultrasonic waves to injection moulding (Fig. 2.4).
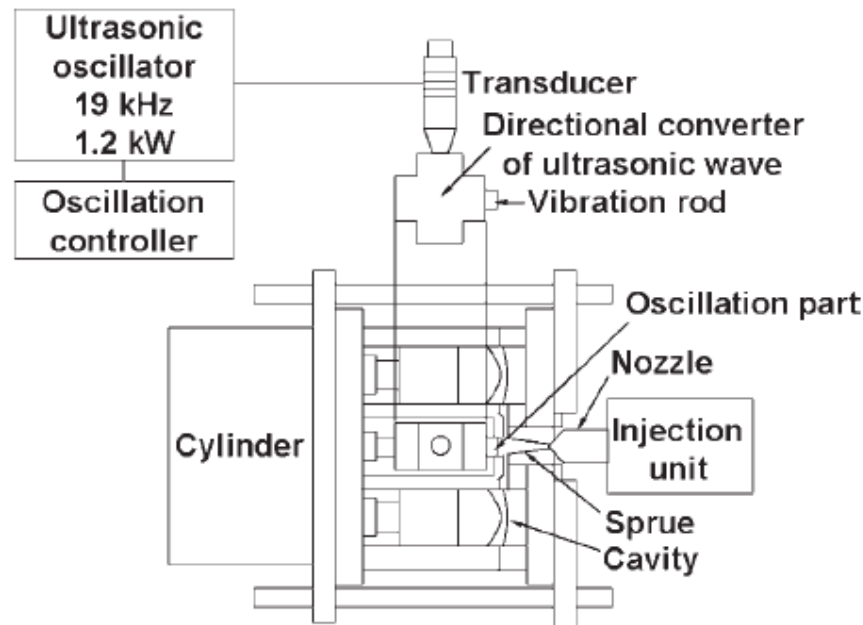
Fig. 2. 4. Schematic of UIM system (Sato et al., 2009).

Results showed that the lens weights produced by UIM with increasing oscillation time up to 20s, were higher than those produced by conventional moulding. Moreover, lens weights increased with increasing amplitude. Regarding the lens surface reproduction accuracy, experiment presented that accuracy of the lens surface was improved by 25% when using UIM compared to the surface produced by conventional moulding.

According to Yang et al. (Yang et al., 2014) ultrasonic oscillation also can reduce the amount of melt pressure lost through the cavity. Results from the investigation revealed that the pressure loss of the flat sample used in ultrasonic assisted injection moulding (UAIM) was approximately 29% lower than that of the sample used in conventional injection moulding. In addition direct oscillation affected on the average residual stress, which contrary to the conventional injection moulding was reduced by 27%.

Jiang et al. (Jiang, 2015) based on physical visualized technology developed a new visualization device to understand behaviour of polypropylene (PP) which melts flowing in ultrasonic assisted injection moulding. Results presented that the higher melts flow velocity can be observed in the middle and near the entrance of the cavity, while low at the end of cavity. Moreover, ultrasonic vibration reduce melts viscosity. By ascending of ultrasonic power, the performance of polymer material is changed, which influences on the final quality parts.

Later on the same device and method was used to analyse the influence of ultrasonic vibration on the velocity of the filling front and the velocity distribution of a PP melt within a cavity. Experiment showed that improving the filling front velocity up to 27 % when used 200W of ultrasonic power and more uniform velocity distribution (Jiang et al., 2017).

An innovative approach to the polymer replication of high aspect ratio micro-structured surface showed Liu et al. (Liu et al., 2018). They introduced new method named ultrasonic vibration micro-injection mould (µVIM) (Fig. 2.5), as a combination of the conventional micro-injection mould and ultrasonic vibration technologies. To compare the replication quality of the microstructures, the mould was designed with two cavities, which were used ultrasonic vibration method and the injection-compression method respectively.
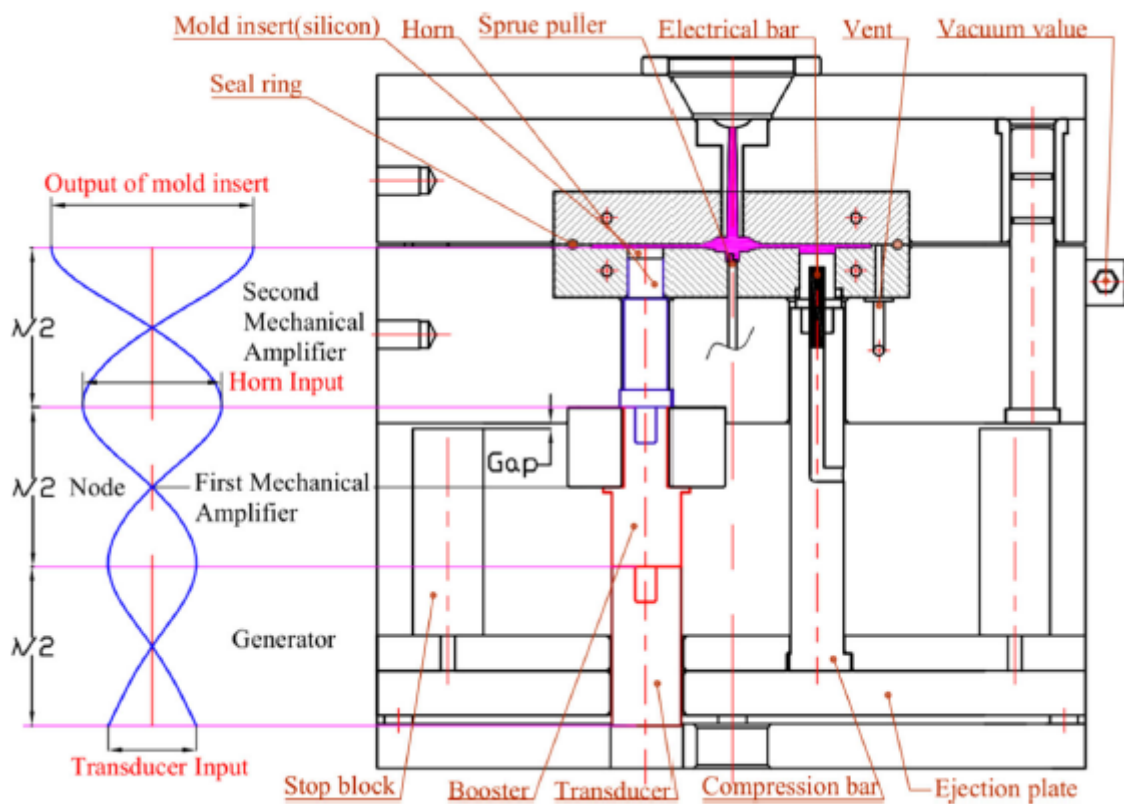
Fig. 2. 5. Sketch of designed mould (Liu et al., 2018).

Experiment focuses on the method and the quality evaluation of filling polymer into the micro channels (Fig. 2.6). Results show that the replication quality of the microstructure initially increased rapidly but then decreased together with the increase of the injection speed and packing pressure. When the packing pressure is too high, the adhesion between polymer and cavity was observed, which cause difficulties during demoulding. Comparing results of µVIM and µICM methods, the µVIM has an advantage on polymer replication of high aspect ratio micro structure. Using novel technology, the average height is increased by about 14.6%. Considering microstructure uniformity, both methods are comparable.
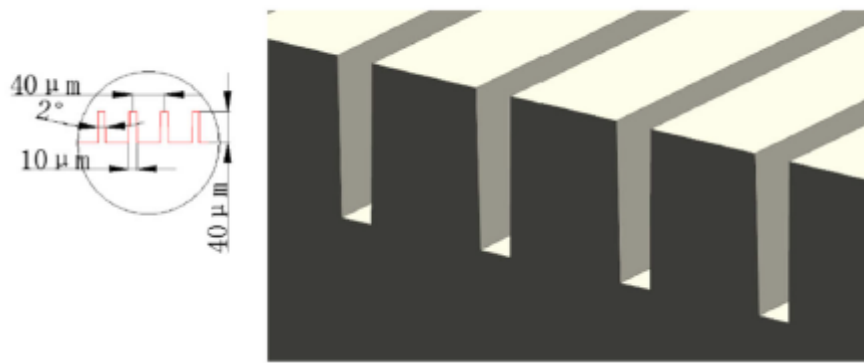
Fig. 2. 6. Micro channels (Liu et al., 2018).

It is important to emphasize that the use of ultrasound in the micro-injection process also affected the properties of the weld line strength. Lu et al. (Lu et al., 2006) by his experiments proved improvement of weld line strength of injection-moulded polystyrene (PS) and polystyrene/high-density polyethylene (PS/HDPE) blends parts. Due to perform the experiments, the ultrasonic oscillation were induced to injection moulding process by laboratory developed special mould (Fig. 2.7).
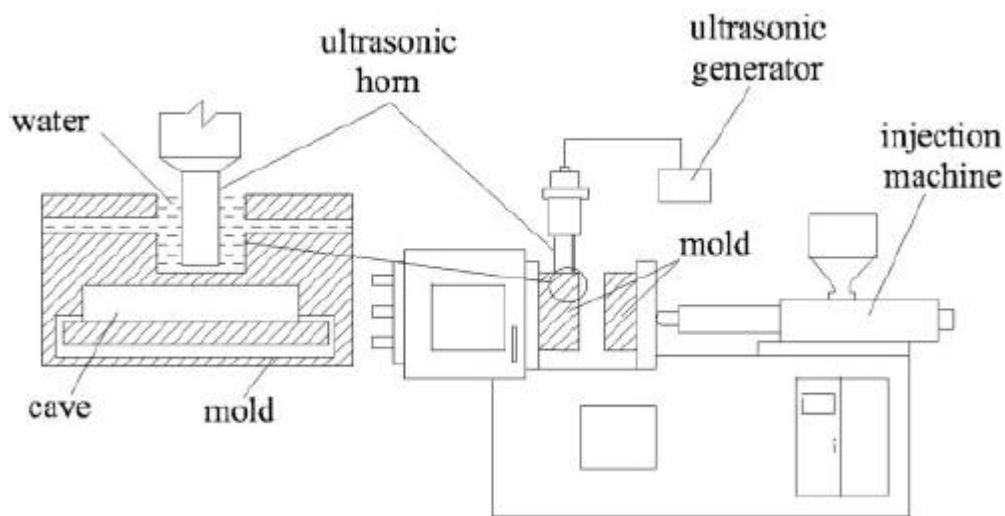
Fig. 2. 7. Schematic diagram of injection and mould with ultrasonic oscillation system (Lu et al., 2006).

As shown in Figure 2.8, ultrasonic oscillation had a great influence on the tensile strength both of PS and PS/HDPE specimens with weld line in the way that enhanced it. Compared with the Mode I (ultrasonic oscillation were induced for whole process of injection moulding), Mode II (ultrasonic oscillation were induced after injection mould filling) gave better results.
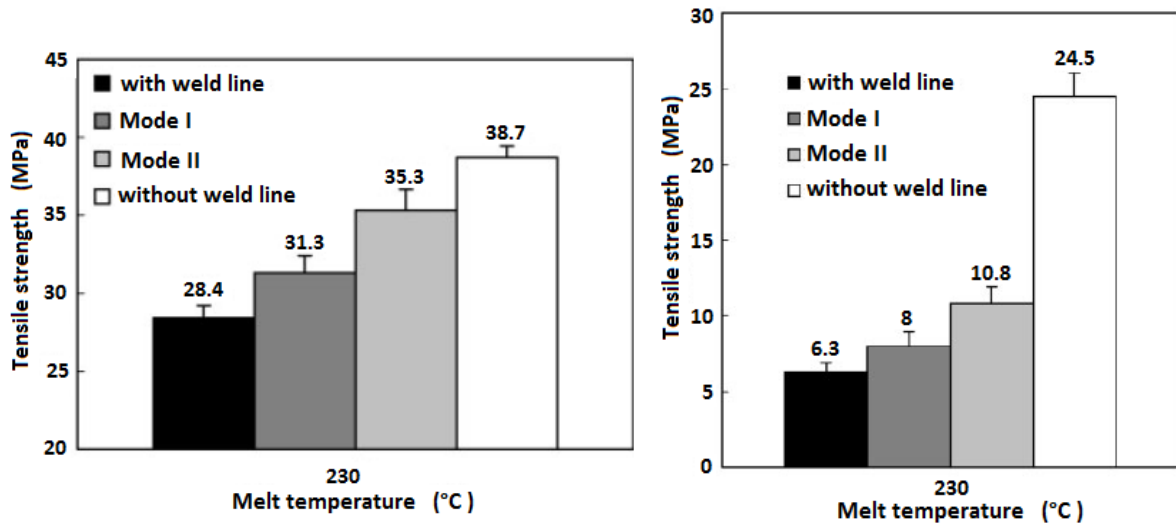
Fig. 2. 8. Effect of ultrasonic oscillation on the tensile strength of: PS (left) and PS/HDPE (right) (Lu et al., 2006).

2.3. Ultrasonic micro-moulding technology

Ultrasonic micro-moulding technology, as a modern technology, reveals quite different way to manufacture micro polymeric parts. With its benefits could be an alternative for low-series micro components production from sensitive and expensive polymers.

2.3.1. Ultrasound technology

The ultrasonic wave is a mechanical wave with a frequency above 20 kHz. An ultrasonic vibration system usually consists of ultrasonic generator, converter, booster and sonotrode (Fig. 2.9).
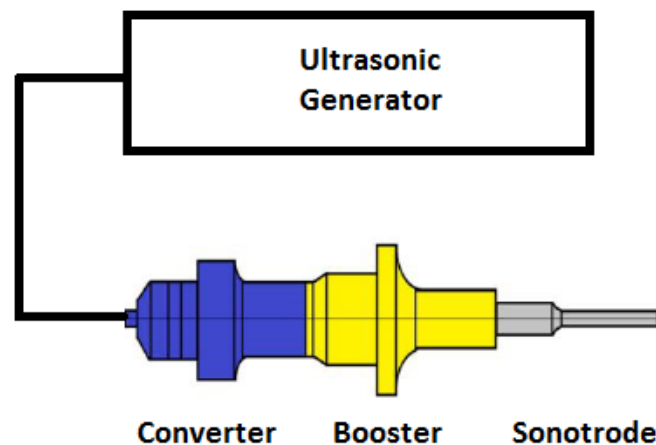
Fig. 2. 9. Ultrasonic equipment.

The ultrasonic generator converts an incoming tension of 220V and 50 Hz into ultrasonic frequency. Converter or transducer transform high frequency electrical signals into mechanical vibration due to the piezoelectric effect. Then the booster modify the incoming amplitude received from transducer. The energy of ultrasonic wave is based on the square of amplitude, so to obtain ultrasonic wave with high energy it would be necessary to amplify the amplitude. Sonotrode is a metallic component which works according to the linear propagation laws.

2.3.2. Ultrasonic plastification

Plasticizing using ultrasounds is based on the fact that ultrasonic wave produces mechanical work during its propagation. Ultrasonic propagation and interaction characteristics are combined with the fundamental mechanical and thermal properties of the material. Thus, vibration energy is absorbed by the polymer in the form of heat, which consequently leads to its melting (Ensminger and Bond, 2012; Grewell and Benatar, 2007).

As the first one in 2002, the potential in using ultrasounds for plasticizing polymeric material was introduced by Michaeli et al. (Michaeli et al., 2002). During the work on the prototype of micro injection-moulding machine (Spennemann, 2000), he proposed new plastification unit (Fig. 2.10.) as a solution to the problem of low plasticising efficiency.
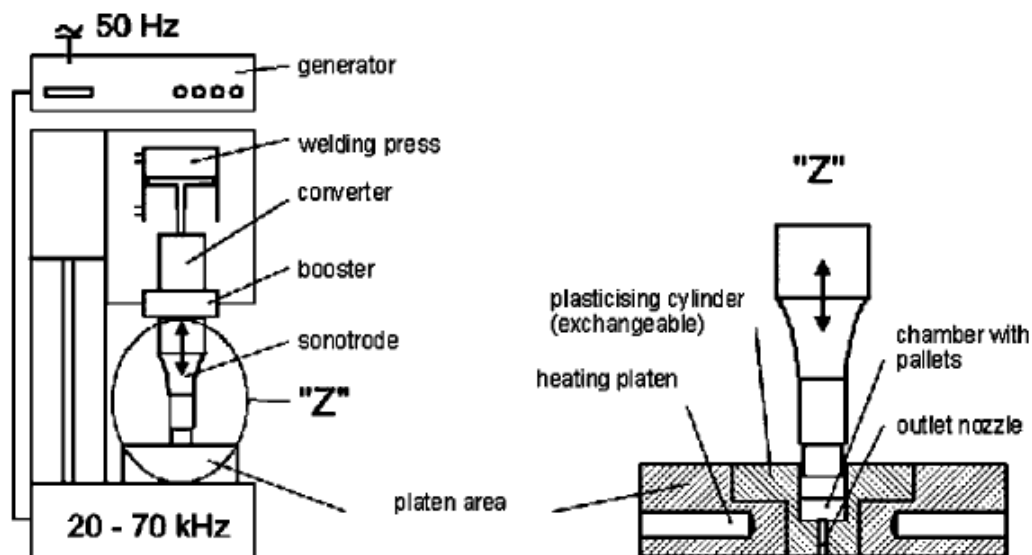
Fig. 2. 10. Ultrasonic plastification unit (Michaeli et al., 2002).

Experiments confirmed high performance of the unit, where during the 5 s was plasticised up to six times more material than necessary for a typical micro part. Also properties of the ultrasonic moulded part characterised by good properties. This contribution encouraged more researchers to work on the subject.

Jiang et al. (Jiang et al., 2009) analysed the mechanism of the ultrasonic plastification of HDPE polymer. For this purpose the ultrasonic plastification testing equipment, built of ultrasonic vibration system and polymer ultrasonic testing inclusive plastification and rheology testing loading module, barrel temperature closed-loop control module, data measure and acquisition module was developed. Performed experiments carried out the conclusion that the melting mass increases with the ultrasonic vibration time and the melt are more homogenized due to mixing action of ultrasonic vibration and wave flow compared with conventional heating plastification. Furthermore, HDPE materials treated by two plastification methods, both exhibit spherocrystal, but in different size (Fig. 2.11).
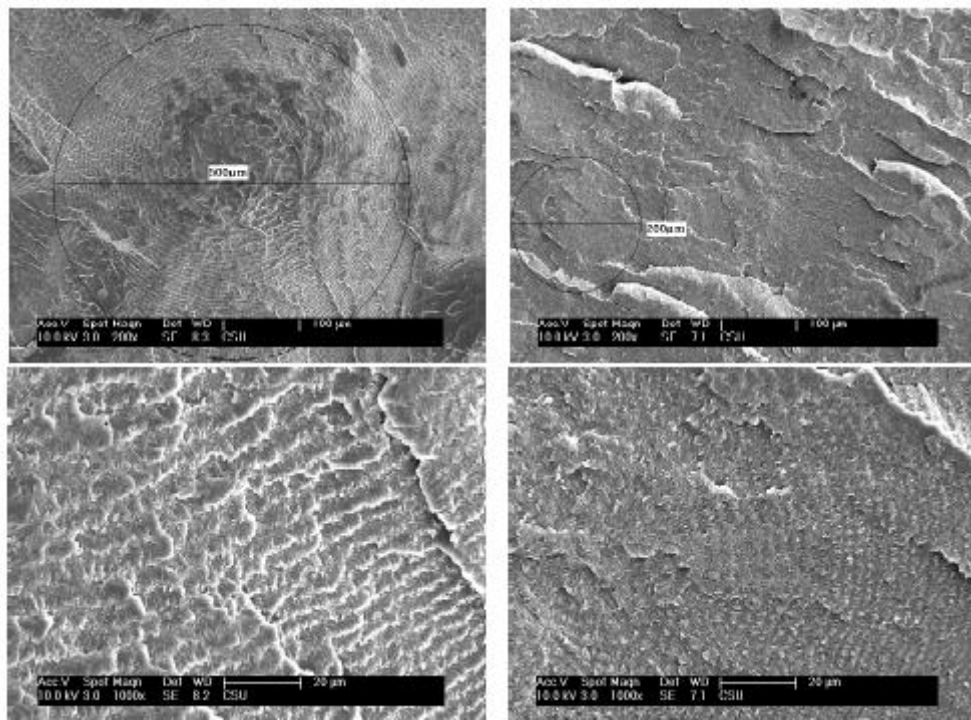
Fig. 2. 11. . SEM of samples' cross sections from heating (left) and ultrasonic plastification (Jiang et al., 2009).

In ultrasonic plasticised sample, the diameter of the spherocrystal was about 200 μm, 300 μm smaller and had more finer and uniform microstructure than the sample from conventional plastification method.

2.3.3. Ultrasonic heating phenomena

To take full advantage of the possibilities offered by ultrasound in the melting of polymeric materials, it is necessary to understand the mechanism of heat generation during the plastification process. Based on Jiang (Jiang et al., 2012) polymer initially is melt because of interfacial friction and volumetric or viscoelastic heating, but when the polymer beneath sonotrode is melted, the ultrasonic cavitation took place.

Wu et al. (Wu et al., 2017) by experimental and numerical methods studied the interfacial friction heating in ultrasonic plasticizing of polymethyl methacrylate (PMMA). The results showed that it is a transient process combined with the extremely fast temperature increasing (61.3 °C in 0.02 s and 160.8 °C in 0.078 s). Moreover, the transient interfacial friction heating coupled with low heat conduction coefficient of polymeric materials lead to temperature concentration in a small area between two granulates. Amplitude parameter had a significant influence on interfacial friction heating what confirmed both the simulation and experimental results. The increase of ultrasonic amplitude from 10 to 30 µm cause an increase of the average heating rate from 460.4 to 1687.5 °C, when polymer granulate were plasticized from 30 to 160 °C (Fig. 2.12).
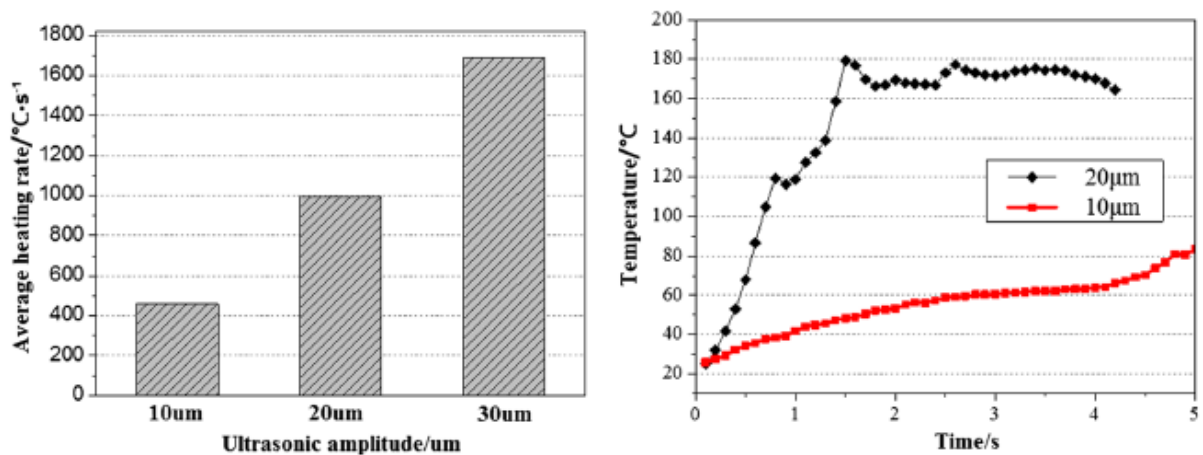
Fig. 2. 12. Calculated average heating rate (left) and experimentally measured temperature curved (right) (Wu et al., 2017).

Regarding influence of plasticizing pressure on the interfacial friction heating, experimental results are different from simulation ones. Although simulation indicated an increase of the average heating rate from 804.2 to 1187.5 °C during increase of plasticizing pressure from 200 N to 800 N, the experiment did not confirm it. Contrary to the simulated results, the increase of plasticizing pressure lead to a decreased average heating rate (Fig. 2.13).
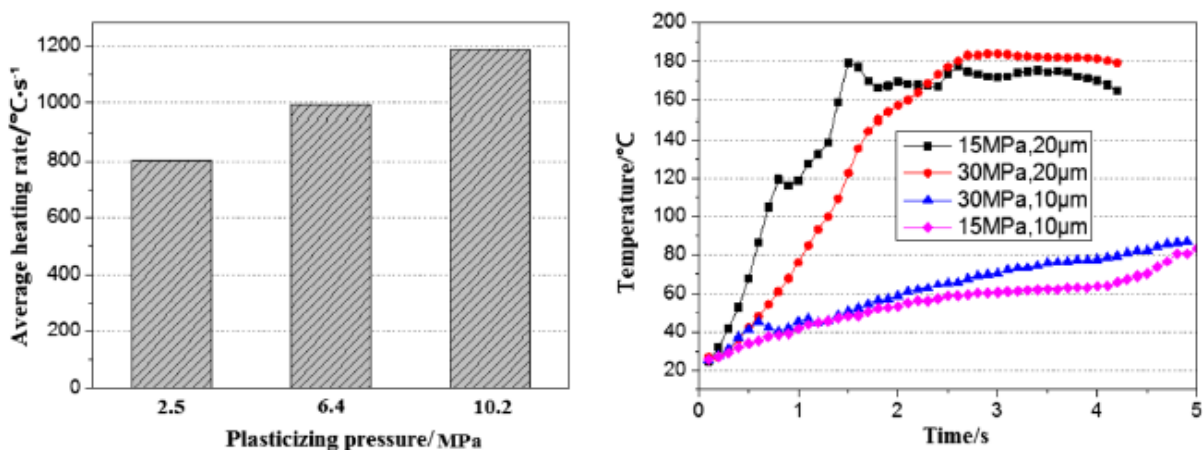
Fig. 2. 13. Influence of plasticizing pressure on the interfacial friction heating: calculated average heating rate (left) and experimentally measured temperature curved (right) (Wu et al., 2017).

Next research exploring the viscoelastic heating mechanism of PMMA in ultrasonic plasticizing process was carried out by Jiang et al. (Jiang et al., 2016). The influence of parameters, such as initial temperature of the polymer, the ultrasonic frequency and the ultrasonic amplitude on the viscoelastic heating rate were investigated theoretically and experimentally. Both the outcomes from simulation and experimentation showed that the heat generation rate can be significantly influenced by the initial temperature, and ultrasonic amplitude compared to the frequency, it affects more on this phenomena. The heating rate of the amplitude value of 30 μm was 2.5 times higher than the one of 10 μm. Furthermore, until the initial temperature rises to the 105 °C there is no significant change in viscoelastic heating rate (Fig 2.14).
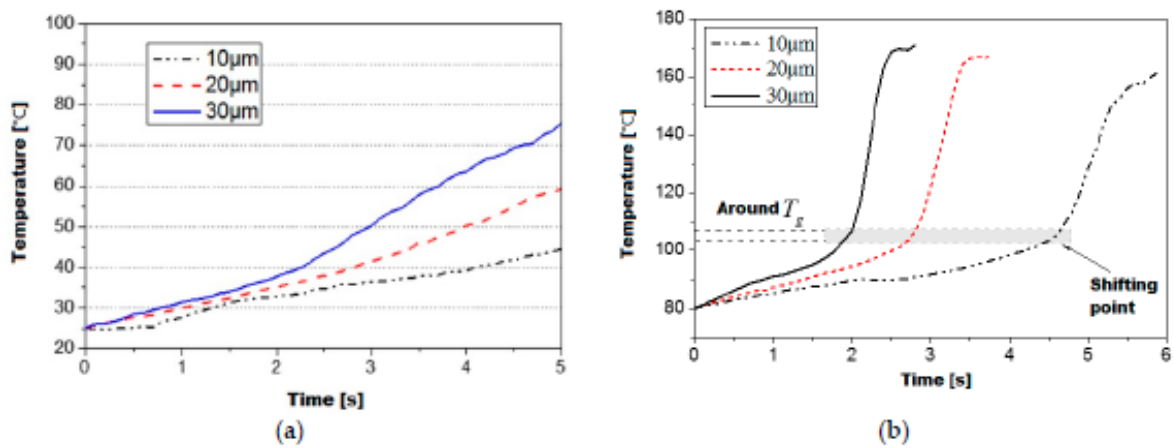
Fig. 2. 14. Measured viscoelastic heating curve: a) initial temperature of 25 °C and b) 80 °C (Jiang et al., 2016)

The third heat effect responsible for melting the polymer is cavitation. A phenomenon that involves the formation of cavities or voids in a molten polymer. Known as cavitation bubbles will grow in size until finally collapse (Mason and Lorimer, 2002). At the point of collapse the temperature of the vapour within the bubble can get even from 2000 to 3000 °C and stresses at 1000 MPa. Jiang et al. (Jiang et al., 2012) stated that ultrasonic cavitation effect has a stronger effect on ultrasonic plastification process than other heat effects including friction and viscoelastic. During research on the influence of process parameters on ultrasonic plastification speed, he found a relationship between pressure and ultrasonic cavitation effect. The experimental results showed that ultrasonic speed of polymer increases with ultrasonic supply voltage and plastification pressure to the maximum value of 0.111 1 g/s.

2.3.4. Ultrasonic micro-moulding process

The ultrasonic micro-moulding process presented in the literature vary in the equipment used, but the principle is the same and may be divided into three steps shown in Figure 2.15.
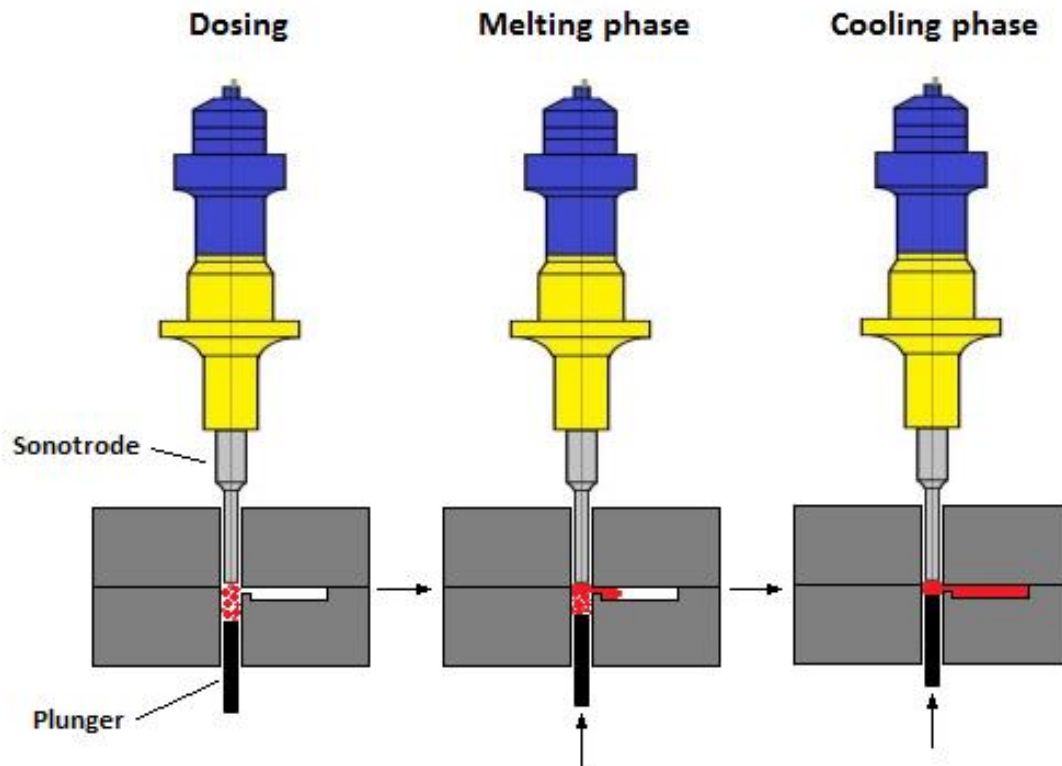
Fig. 2. 15. Ultrasonic micro-moulding process.

First, the required amount of the pellet is putting into the chamber of the mould. Then the plunger moves toward the vibrating sonotrode compressing the polymer content. Due to the thermal energy, polymer starts to melt and fills the cavity. At the last step the filled melt solidifies and is ejected as desired shape micro part.

2.3.5. Ultrasonic micro-moulding process parameters

Acquiring knowledge about process parameters of ultrasonic micro-moulding process, and how they affects on the final product properties, is one of the most important factors affecting stable and effective production of micro elements. This knowledge is still insufficient, however, there are some works explaining the impact of particular parameters on the polymers parts.

Michaeli et al. (Michaeli et al., 2011) by investigation carried out on PP polymer proved that amplitude value impacts not only on plastification process but also on the mixing effect. The amplitude of 29.4 μm was introduced as the minimum value required to completely fill a tensile bar. Moreover, higher amplitude supported an improved quality of mixing effect, making the colour of the specimen more homogeneous (Fig. 2.16). Regarding impact of amplitude and compression force parameters on the shot weights, they found only a small effect.

amplitude: 29.4 µm
compression force: 300 N

amplitude: 49.0 µm
compression force: 300 N

2 mm
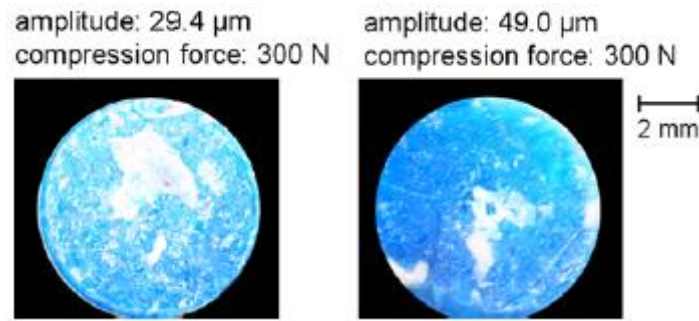
Fig. 2. 16. Effect of the mixing of PP powder during the ultrasonic plastization (Michaeli et al., 2011).

Later on, Zeng et al. (Zeng et al., 2014) found a relationship among ultrasonic time, pressure and flash thickness. Micro-ultrasonic powder moulding (micro-UPM) process were utilized to manufacture at least five specimens from different set of parameters. Ultrasonic time varied from 1.0 to 7.0 s, while pressure value was 0.1, 0.2 and 0.4 MPa, respectively. The results showed that increasing ultrasonic amplitude under constant pressure, causes thinning of the flash to the moment, when the flashes automatically separate from the micro part. Furthermore, the samples fabricated from optimum set of parameters in micro-UPM was characterised by 6.9% higher tensile strength value and 70.1% lower elongation at break than the properties of the samples made from injection moulding.

The effects of the ultrasonic process parameters has on the physical and chemical properties of the polylactide (PLA) was presented by Sacristán et al. (Sacristán et al., 2014). Conducted optimization of ultrasonic amplitude and moulding pressure, allowed to specify two sets of parameters from which, homogeneous samples can be achieved. The best samples had the same thermal stability and mechanical properties as samples processed by conventional moulding techniques.

In another research, Planellas et al. (Planellas et al., 2014) optimized process parameters, such as amplitude, moulding pressure and ultrasonic time due to obtain good moulding efficiency and minimum degradation of specimens. The use of appropriate conditions, both for PLA and PBS samples, has led to manufacture samples with a number average molecular weight decrease lower than 6%.

The influence process parameters (e.g. humidity of the pellets, sonotrode velocity, and mould temperature) in ultrasonic micro-moulding have on filling cavity, porosity, part weight and dimension o PP parts was investigated by Negre et al. (Negre et al., 2015). Their results confirmed that by drying polypropylene granulates, parts with reduced porosity and increased dimensional accuracy are obtained. It was also observed that ultrasound exposition time of 3 s allowed to fill completely the mould cavity. Finally, pressure applied to melting process influence on the weight and dimensions of the moulded parts in such a way that by its increase results in better mouldings.

Later, a relationship between the processing conditions on the final polyamide (PA12) product was demonstrated by Grabalosa et al. (Grabalosa et al., 2016). Their presented that the part of 300 mg weight could be plasticized and injected in less of 3 s and its quality could be improved by increasing values of applied pressure, ultrasonic vibration time and amplitude. Furthermore, FTIR analysis showed that increasing duration of ultrasonic time does not cause chemical degradation of PA12. Additionally, the same analysis was conducted on injection, centre and raw region of specimen processed at the longest vibration time and again, no changes in the chemical structure are observed.

Next polymer material processed in ultrasonic micro-moulding technology and how involved process parameters influence on the structure, degradation and mechanical properties of ultra-high-molecular-weight polyethylene (UHMWPE) was reported by Sánchez-Sánchez et al. (Sánchez-Sánchez et al., 2017). An analysis of variance (ANOVA) was used to investigate the effects of four process parameters (amplitude, initial shape of the raw UHMWPE specimens, plunger velocity profile and mould temperature). Results showed that higher amplitude and a mould temperature of 100 ℃ provided better filled samples. Plus, using irregular shapes of specimens rather than circular also led to better results. Mechanical properties of the processed specimens were improved due to the effect of the high degree of crystallinity. Regarding thermal stability, it was not significantly influenced by the decrease in the molecular weight, what was showed by TGA analysis.

As seen above all of the processed materials are related to the commodity and engineering polymers. Until now, there is no research about ultrasonic micro-moulding processing of materials that belong to high performance polymers.

2.4. High performance polymers

High performance polymers (HPPs) are classified at top of the list of all available of polymeric materials due to their outstanding properties. They also are named as high temperature polymers and are considered to have a short-term heat resistance of 250 ℃ and can withstand long-term heat resistance of 160 ℃. Moreover, HPPs are characterized by other distinguishing features include their high strength and stiffness, resistance to chemicals and their electrical properties (Platt, 2003). As seen on the example in Figure 2.17 the price of the polymers increases together with the properties that characterize them.
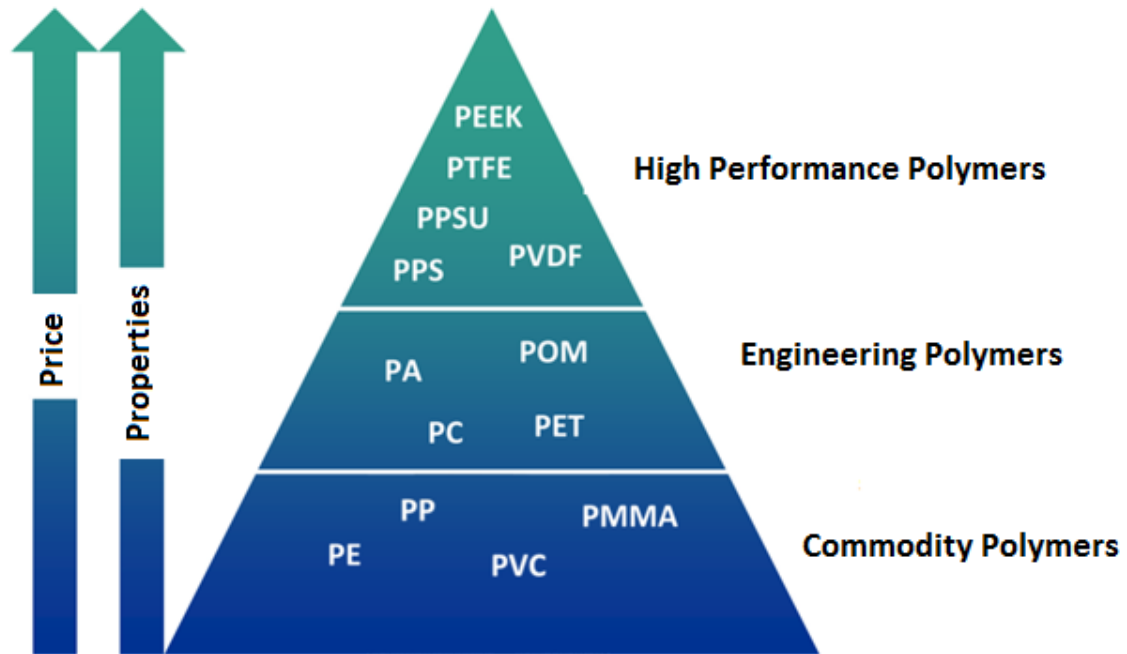
Fig. 2. 17. Polymers classifications.

2.4.1. Polyphenylsulfone (PPSU)

Polyphenylsulfone is transparent, hydrolytically stable, amorphous thermoplastic. The chemical structures are presented in Figure 2.18 whilst mechanical and thermal properties in Table 2.1.
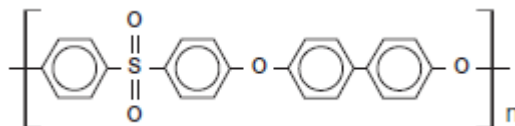
Fig. 2. 18. Radel® PPSU chemical structure (Solvay, 2014).

Table 2. 1. Radel® PPSU properties (Solvay, 2014)

Property	Unit	Radel R-5500
Mechanical		
Tensile strength	MPa	70
Tensile modulus	GPa	2.34
Tensile elongation		
at yield	%	7.2
at break	%	60-120
Flexural strength	MPa	105

Flexural modulus	GPa	2.41
Compressive strength	MPa	99
Shear strength	MPa	61
Izod impact strength		
notched	J/m	694
unnotched	J/m	no brake
Tensile impact	kJ/m2	400
Rockwell hardness		R122
Thermal		
Heat deflection temperature		
at 0.45 MPa	^{o}C	214
at 1.82 MPa	^{o}C	207
Thermal expansion coefficient	μm/m^{o}C	56
Thermal conductivity	W/m K	0.30
Glass transition temperature	^{o}C	220

Its hydrolytic stability allows him to use in applications that require repeated numbers of steam sterilization while stiffness, rigidity, toughness, chemical and high heat resistance make its attractive for the production of high-performance products, especially for medical sector. The polymer is suitable choice for the products, e.g.: heart valve transportation unit, medical drawers, dental picks and trays (Sastri, 2014). Furthermore, it is also widely used as a membrane material for water reuse or solvent nanofiltration applications (Darvishmanesh et al., 2011; Feng et al., 2016; Liu et al., 2016; Nayak et al., 2017).

2.4.2. Polyetheretherketone (PEEK)

Polyetheretherketone is a semi-crystalline processable material with a unique combination of properties (Tab. 2.2). The most important are: exceptional chemical resistance (organics, acids and bases), high mechanical strength at temperature in excess of 250 ^{o}C, excellent wear and abrasion resistance, best-in-class fatigue resistance, excellent resistance to hydrolysis in boiling water and superheated steam, low moisture absorption and high purity. The chemical structures of the polymer is shown in Figure 2.19.
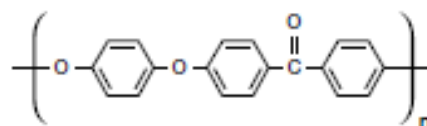
Fig. 2. 19. KetaSpire® PEEK chemical structure (Solvay, 2013)

PEEK can be used in very demanding applications as a replacement for metal. With the trend towards higher operating temperatures and miniaturization, plastic replacing metals also offer

weight and noise reduction. The main markets are: automotive, aerospace, food processing industry, electronics and medical.

Table 2. 2. KetaSpire® PEEK properties (Solvay, 2013)

Property	Unit	KetaSpire KT-820 NT
Mechanical		
Tensile strength 50mm/min	MPa	95
Tensile modulus 50mm/min	GPa	3.5
Tensile elongation		
at yield 50mm/min	%	5.2
at break 50mm/min	%	20-30
Flexural strength	MPa	147
Flexural modulus	GPa	3.7
Compressive strength	MPa	118
Shear strength	MPa	84
Izod impact strength		
notched	J/m	91
unnotched	J/m	no brake
Thermal		
Heat deflection temperature		
at 1.82 MPa	^{o}C	157
Melting point	^{o}C	340
Thermal conductivity	W/m K	0.24
Glass transition temperature	^{o}C	150

The most important benefit of PEEK polymer in automotive are enhanced dry and lubricated surface interaction, outstanding mechanical properties in a wide temperature range and excellent fatigue properties. Thus, the polymer are used in applications like: piston units, seals, washers and bearings. Applications for PEEK in the aerospace include critical engine parts, interior components and electrical systems protection. In food processing equipment the material is common used to industrial coffee machines, food pump seals and automatic espresso machines. In medical sector PEEK polymer is successfully replacing glass, stainless steel and other metals (Platt, 2003). Material is used not only to instruments but due to its biocompatibility, it also use in human implants applications (Jaekel et al., 2011; Kurtz and Devine, 2007; Maldonado-Naranjo et al., 2015; Najeeb et al., 2016; Schwitalla et al., 2015, 2016; Toth et al., 2006).

2.5. Summary of the State of the art

Table 2.3 summarizes the principal fields, authors and contributions, which were taken into account while working on the Thesis.

Table 2. 3. State of the art summary

Fields of work	Author	Year	Contributions
Micro-injection moulding process	Chang et al.	2007	Prototype of external-type microinjection moulding module for thermoplastic polymer
	Oyetunji	2010	Prototype of the small injection moulding machine.
	Bloß et al.	2014	Prototype of two-step plunger system dedicated to small shot volumes.
Ultrasonic assisted injection	Lu et al.	2006	Analysis of the effect of melt temperature and ultrasonic oscillations on weld line strength of PS and PS/HDPE blend.
	Lee et al.	2008	Numerical analysis of the ultrasonic vibration effect during injection moulding filling process.
	Sato et al.	2009	Study of ultrasonic wave to injection moulding process using developed ultrasonic injection moulding system.
	Yang et al.	2014	Characteristics analysis and mould design for ultrasonic-assisted injection moulding.
	Jiang et al.	2015	Analysis of PP behaviour during melt flow in ultrasonic assisted injection moulding.
	Jiang et al.	2017	Analysis of the influence of ultrasonic vibration on the velocity of the filling front and the velocity distribution of a PP melt within a cavity
	Liu et al.	2018	New method named ultrasonic vibration micro-injection for the polymer replication of high aspect ratio micro-structured surface
Ultrasonic plastification	Michaeli et al.	2002	Novel ultrasonic plastification unit.
	Jiang et al.	2009	Analysis of the mechanism of the ultrasonic plastification of HDPE polymer.

Ultrasonic heating	Jiang et al.	2016	Analysis of the viscoelastic heating mechanism of PMMA in ultrasonic plasticizing process
	Wu et al.	2017	Experimental and numerical analysis of the interfacial friction heating in ultrasonic plasticizing of PMMA.
Ultrasonic micro-moulding process	Michaeli et al.	2011	Analysis the effects of process parameters on the shot weight of PP and mixing effects in ultrasonic plasticization and direct injection process.
	Zeng et al.	2014	Analysis the process and properties of micro-ultrasonic powder moulding with PP.
	Sacristán et al.	2014	Analysis the effects of ultrasonic vibration on the micro-moulding of polylactide
	Planellas et al.	2014	Optimization of ultrasonic processing parameters to obtain minimally degraded sample of PLA and PBS.
	Negre et al.	2015	Study of ultrasonic moulding process parameters for manufacturing PP parts.
	Grabalosa et al.	2016	Analysis the influence of processing conditions on manufacturing polyamide parts by ultrasonic micro-moulding.
	Sánchez-Sánchez et al.	2017	Study of ultrasonic micro-injection process of UHMWPE.

Chapter 3. Effect of the main process parameters on the mechanical strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process

Chapter 3 presents study of the processing window and dependence between the process parameters, such as amplitude, plunger velocity and ultrasonic exposure time and their influence on the mechanical properties of PPSU samples.

This study was presented in an article entitled: *"Effect of the main process parameters on the mechanical strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process"*, published by Ultrasonics Sonochemistry in April 2018 (Dorf et al., 2018).

Effect of the main process parameters on the mechanical strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process

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ARTICLE INFO

ABSTRACT

Ultrasonic micro-moulding technology was used to process high performance polymer polyphenylsulfone (PPSU) due to investigate mechanical and chemical characteristics of manufacturing parts. Both the processing window and dependence between the main input parameters, in this case amplitude, plunger velocity and ultrasonic exposure time and their influence on the mechanical properties were appointed. The experiments showed that each available amplitude level (58 μm, 52.2 μm, 46.4 μm, 40.6 μm) are suitable to produce specimens characterised by high mechanical strength but only when combined with the appropriate values of the rest of the parameters. The parameter, which influenced the most on the part degradation is the ultrasonic vibration time. Samples from the combination of parameters, where the amplitude and velocity had the highest value but time of sonication is one of the lowest are less exposed for degradation. Cavitation bubbles makes polymer falling apart which decreases mechanical strength of the manufacturing parts. Degradation was observed via FTIR analysis even if it was not visually visible. Finally, the model as a tool for selecting the appropriate values for the input process parameters when using the novel ultrasonic micro-moulding technology required to produce PPSU parts characterised by their high mechanical strength was developed.

1. Introduction

Ultrasonic vibration (> 20 kHz) as an environmentally-benign technique is broadly used in a large number of fields. Advantages such as speed and easiness of use as well as easiness of control makes ultrasonics very interesting and important subject to further investigation by the researchers. The ultrasonic usefulness can be considered in terms of low-intensity and high-intensity applications, which are constantly develop. In the low-intensity applications the transmitting energy never change the state of the medium after the wave has propagated through it. As examples of such applications, we can distinguish: characterization and measurements of materials, medical diagnosis and marine [1–9]. High-intensity applications can be define as those which effect on or produce the changes in a medium of propagating. This category includes: sonochemistry, sonoluminescence, sorting and particle motion in fluids, emulsification and welding of plastics [10–18].

In recent years, an alternative technology for producing micro parts using an ultrasonic vibration as the source of energy to melt polymers has become available. This technology is characterised by the ability to process only the material needed for one cycle and so would appear to be a good option for processing expensive polymers in low-volume production.

In 2002, W. Michaeli et al. [19] reported on the ability to plasticize polymer materials using ultrasonic energy. Their project described a prototype for a new microinjection-moulding machine that would decrease the minimum shot weight [20]. In the first step of the project, they were able to reduce the sprue to about 15 to 20 mg. The second step then focused on improving the existing plastification system. In the initial version, where a small amount of material was plasticized in an electrically heated cylinder, the melting time proved unacceptable. To make the whole process more cost-effective, they proposed using ultrasonic energy to plasticize the material. The subsequent experiments showed the concept to be highly efficient – not only a very short dosing time was achieved, but also a homogeneous polyoxymethylene (POM) structure. These advantages encouraged additional research work to further develop the new technology for new materials.

While almost all commercially available polymeric materials dedicated to standard injection moulding processes come with guidelines on standard processing conditions, there are none on how to process the material using ultrasonic micro moulding technology. Therefore, as new polymeric materials are developed it is important to constantly study them and review the guidelines and, if need be, update the

processing conditions for these new materials and the influences they may have on a part's properties. Currently there is some research in the literature which explains process parameters and their influence on selected properties of the polymeric parts. This can also be useful for successful processing with ultrasonic technology.

Researchers are interested in polypropylene (PP) as it is one of the most commonly-used materials to produce plastic components. Michaeli et al. [21] established that the amplitude value impacts both the plastification process and the mixing effect. Trials conducted with an experimental machine showed that a minimum value of 29.4 μm is required to completely plasticize the amount of polymer required to fill a tensile bar. Furthermore, a higher amplitude improves the mixing quality, making the colour of the specimen more homogenous. They also found that the process parameters, such as the amplitude of the sonotrode and the compression force, had a slight impact on the weight of the part in question. Following on from Michaeli et al., Zeng et. al. [22] found a relationship between the flash thickness and ultrasonic time and pressure. Using a micro-ultrasonic powder moulding (micro-UPM) method, they manufactured specimens by means of different ultrasonic times (from 1 to 7 s) and pressures (0.1, 0.2, 0.4 MPa). Results indicated that under constant pressure, the flash gradually thins with increased ultrasonic time and separates once the critical value is reached. Moreover, the tensile strength value of the samples achieved from the optimum set of parameters for micro-UPM was 6.9% higher than the corresponding properties of the samples made from injection moulding, and the elongation at break was 70.1% lower. The influence process parameters (e.g. humidity of the pellets, sonotrode velocity and mould temperature) in ultrasonic moulding have on filling cavity, porosity, part weight and dimension of polypropylene parts was examined by Negre et al. [23]. Their results showed that drying the pellets decreases porosity and improves dimensional accuracy. The specific ultrasound time (3s) allowed complete parts to be obtained and the amount of time could be increased when using velocities lower than 7 mm/s.

The effects ultrasonic vibration has on the physical and chemical properties of polylactide (PLA) micro-moulding processing was described by Sacristán et al. [24]. In their research work, they optimised ultrasonic amplitude and moulding pressure and reported that only two moulding pressure/ultrasonic amplitude combinations led to completely filled homogenous specimens being obtained. The best samples (at a 48.1 μm amplitude with 3 bar moulding pressure) exhibited the thermal stability and mechanical properties comparable to those produced by conventional technology. The SEM micrographs of the surface show that this specimens were transparent and free of holes, which appear as a result of cavitation- inseparable part of ultrasonic moulding process. Cavitation phenomenon and temperature rising induced by ultrasonic waves are two possible reasons of polymers degradation. The third one is the chain scissions caused by mechanical shear stresses. In this paper, PLA degradation was observed, inter alia, by FTIR analysis where peak attributed to the presence of double bounds was detected. Thus, in another research, Planellas et al. [25] optimized three process parameters: time, amplitude and force to obtain good moulding efficiency and minimum degradation of polylactide (PLA) and polybutylene (PBS) samples. They also suggested that degradation also seems to increase for longer irradiation times.

Grabalosa et al. [26] demonstrated that the combination of amplitude, pressure and vibration times directly affects part filling, dimensional accuracy and the mechanical properties of a polyamide part (PA12).). FTIR analysis show that increasing the vibration time does not cause chemical degradation of PA12- there are no new absorption peaks observed. The same analysis was performed on injection, centre and raw region of specimen processed at the longest vibration time and again, no evidence of changes in the chemical structure are registered. Contrary to the previous papers mentioned here, Grabalosa et al. report that parts processed with lower ultrasonic time tend to have more defects.

The processing technique for producing a well-filled miniaturized dog-bone shaped specimen and the influence of the processing parameters on the structure, degradation and mechanical properties of ultra-high-molecular-weight polyethylene (UHMWPE) were investigated by Sánchez-Sánchez et al. [27]. They indicated that the degree of crystallinity of processed UHMWPE specimen, was higher than that of an untreated UHMWPE specimen which, in turn, results in improved mechanical properties. GPC analysis showed a decrease in the molecular weight of the specimen, which was associated with ultrasonic degradation owing to polymer chain scission. The greatest decrease was reported when 100% amplitude was applied. Furthermore, thermogravimetric (TGA) analysis showed that the thermal stability of the fabricated samples was not significantly influenced by the decrease in their molecular weight.

Although some studies on ultrasonic micro-moulding technology using the knowledge about thermoplastic materials processed so far have been undertaken, the majority are limited to commodity and engineering polymers.

In this study, for the first time a PPSU polymer was moulded by ultrasonic energy to produce a reduced-scale specimen. The paper analyses the effect, which main process parameters of amplitude (μm), plunger velocity (mm/s) and the ultrasonic exposure time (s), have on the tensile strength of the polyphenylsulfone (PPSU), with the purpose of aiding process parameter selection based on the mechanical properties required by the product. Furthermore, selected specimens were analysed via FTIR-ATR and SEM for any signs of degradation.

2. Experimental setup

2.1. Material

The Radel® R-5100 GY1137polyphenylsulfoneused in this study is a commerciallyavailable material manufactured by Solvay Ltd. It is a fully aromatic polymer which chemical structure given in Fig. 1 [28]. Parts made from PPSU are characterised by dimensional stability, toughness, good impact and chemical resistance, hydrolytic stability, biocompatibility and exceptional thermal resistance (207 °C). A tensile strength of 69.6 MPa (tested by the ASTM D638 method) and the ability to withstand steam and other high heat sterilization methods makes them an attractive choice for medical devices such as surgical tool trays, nebulizers, humidifiers, flow controls, instrument housings, dental and surgical instruments, fluid containers, heart valve cases, microfiltration apparatus and other kinds of equipment [29,30].

2.2. Micro-moulding processing equipment

The small specimens (complying to the EN ISO 527-2/1BB standard) were manufactured using the Sonorus® 1G Ultrasonic Micro Moulding machine developed by Ultrasion S.L. (Fig. 2) [31]. The ultrasonic head in the machine converts an electrical wave, produced by an electronic ultrasonic generator, into a mechanical vibrating at an ultrasonic frequency of 30 kHz. The heart of the converter is a lead zirconate electrostrictive element which expands and contracts at its resonant frequency when excited by electrical energy. The mechanical vibration is transmitted to a cylindrical component called a sonotrode which, in applying this vibration to the plastic pellets melts them (Fig. 3).
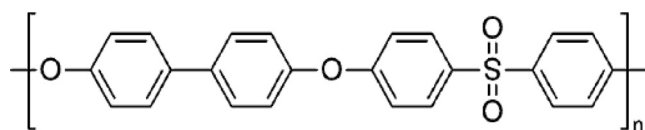
Fig. 1. Chemical structure of PPSU (polyphenylsulfone).
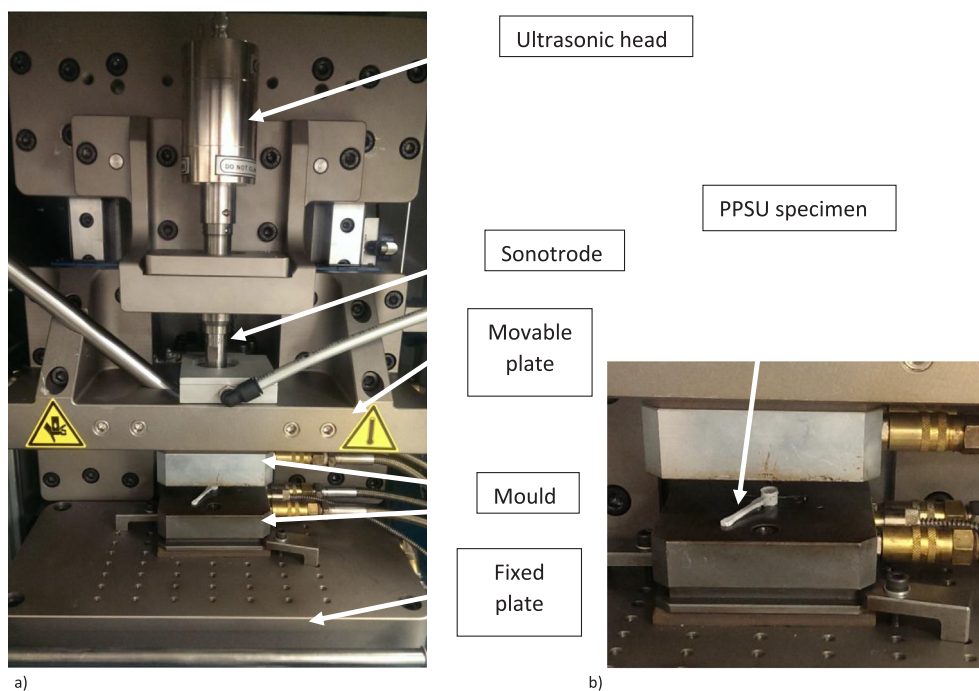
Fig. 2. Experimental setup: a) ultrasonic moulding machine, b) mould and specimen.
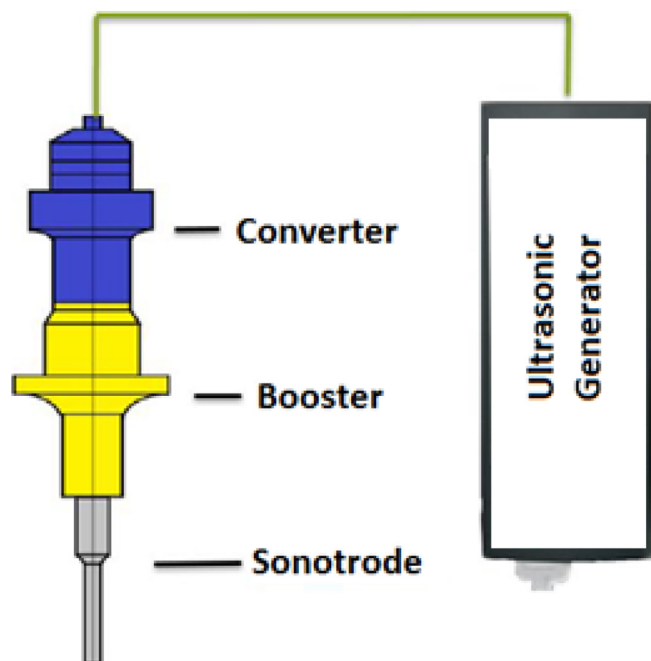
Fig. 3. Ultrasonic equipment.

Vibrations are transformed into the thermal energy (latent heat of fusion) with the way in which the frictional movement occurs between the surfaces that touch each other and the absorption of ultrasonic waves. Then, a moving injection plunger injects the melt into the mould cavity. Once the polymer has solidified, the mould is then opened and the moulded part removed (Fig. 4). To achieve high quality PPSU parts, the temperature of the mould is critical as it is an important factor in determining shrinkage, warpage and the level of moulded-in stresses in the part. The temperature range recommended by the supplier is 138–163 °C and to achieve this the aluminium mould was equipped with an oil circulation flow [32]. As the polymer must be dried to avoid cosmetic defects in the resulting part, the external standard dryer of an

injection moulding machine was used for this purpose.

2.3. Micro-moulding experiments

The experiments were carried out to examine how the main adjustable process parameters, such as amplitude (A), plunger velocity (V) and ultrasonic exposure time (t), affect the tensile strength of the parts. To achieve sufficient data for statistical analysis, the experiment consisted of 196 combinations of the parameters shown in Table 1. From each set of parameters three samples were taken, albeit except in two cases (∗) (∗∗) where the samples were received in smaller quantities (see explanation below Table 1).

The limit values for the process parameters were adopted based on the previous technological trials carried out as screening experiments. The values were:

- *A maximum amplitude* of 58 μm, corresponding to the highest available value in the machine
- *A maximum velocity* of 11 mm/s was accepted as the highest velocity of the plunger which, when combined with the highest available amplitude, the PPSU polymer can be melted and the cavity filled completely (any attempt to increase this value resulted in machine overload, causing a break in the cycle)
- *A maximum ultrasonic exposure time* of 2.8 s is a time taken to cover 14 mm at a velocity of 5 mm/s
- *A minimum amplitude* of 40.6 μm is the lowest amplitude which will cause the PPSU polymer to melt
- *A minimum velocity* of 5 mm/s, corresponds to the highest possible plunger velocity during the process with 40.6 μm amplitude
- *A minimum ultrasonic exposure time* of 1.3 s is a time taken to cover 14 mm at a velocity of 11 mm/s.

Before processing, the polymeric material was dried for 2.5 h at 149 °C in accordance with the supplier's recommendations. The temperature of the mould was set to 145 °C. For each of the mouldings, tensile strength tests were conducted, albeit with the exception of the unfilled mouldings. The results were then used for further statistical analyses. Samples highlighted in Table 2 were analysed by SEM and
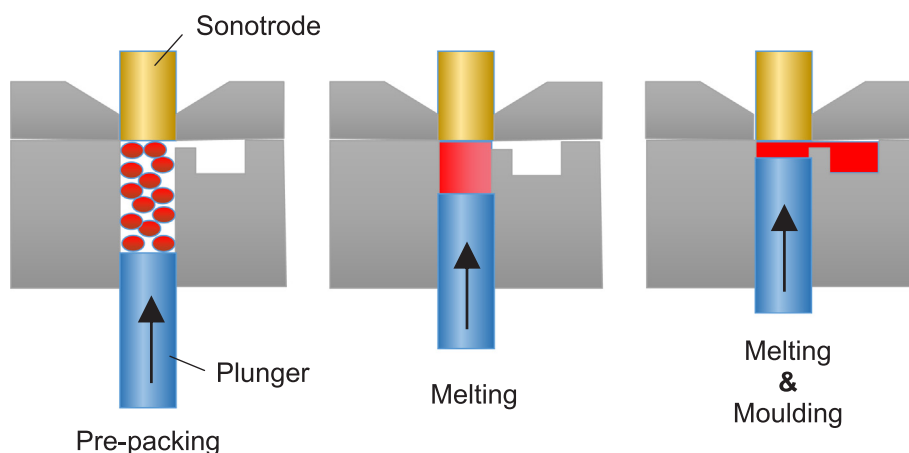
Fig. 4. Scheme of the ultrasonic micro-moulding process.

Table 1
Design of Experiments (DoE).

Parameters	Values						
Amplitude (μm)	40.6		46.4		52.2		58
Velocity (mm/s)	5	6	7	8	9	10	11
Time (s)	1.3	1.4	1.6	1.8	2	2.3	2.8

FTIR-ATR(See Table 3).

2.4. Measurements

Manufactured specimens were tested for tensile strength (σ_M) on the MTS Insight 100kN machine (Fig. 5). Experiments was performed in compliance with the EN ISO 527-2 standard, i.e. with the test speed of 5 mm/min at a room temperature of 23 ± 2 °C. The data equation rate was set to 25 Hz.

Inspection of the morphology of selected samples was conducted by scanning electron microscopy INSPECT 350 from FEI Company. Gold coating was accomplished by using low vacuum coater Leica EM ACE200. Samples were visualized at an accelerating voltage of 25 kV.

FTIR analysis were performed at a resolution of $4\,cm^{-1}$ using diamond attenuated total reflection (ATR) with an infrared spectrometer Nicolet 6700 from Thermo Scientific, equipped with a diamond crystal. The scan frequency ranged from $500\,cm^{-1}$ to $4000\,cm^{-1}$ (32 scans). A background spectrum was run and sample spectra were normalized against it.

Thermal analysis via differential scanning calorimetry measurement was carried out with DSC 200 F4 Maia thermal analyser produced by Netzsch. Specimens with mass about 13 mg were heated from 40 to 400 °C with rate 10 K/min in nitrogen atmosphere.

2.5. Mathematical modelling and statistical analyses

Statistical analysis was performed using Statistica 10 software. As part of the study, basic descriptive characteristics were calculated. The data has been analysed as a whole and divided into groups due to the input parameters. Moreover, using the Shapiro-Wilk test, the data normality was checked.

To create a mathematical model of the ultrasonic micro-moulding process the Marquadt-Levenberg algorithm (LMA) was used. This algorithm combines the conjugate gradients and the Gauss-Newton

Table 2
Tensile strength value for different amplitude σ_M ± s. Highlighted samples were chosen for further investigations – numbers in brackets indicates number of parameters combination.

AMPLITUDE [μm]	VELOCITY [mm/s]	TIME [s]						
		1.3	1.4	1.6	1.8	2	2.3	2.8
58	11	66±4	69±1 (2)	64±2	65±3	64±10	58±18	57±10
	10	-	43±23	51±17	69±1	60±9	52±16	13±23*
	9	-	-	49±15	63±14	62±6	54±15	48±5
	8	-	-	-	39±6	50±11	36±14	41±11
	7	-	-	-	-	40±10	37±17	27±29**
	6	-	-	-	-	41±3	33±7	47±4
	5	-	-	-	-	-	33±10 (48)	40±9
52.2	9	-	-	-	-	69±1	68±2	62±5
	8	-	-	-	-	67±1	68±2	67±2
	7	-	-	-	-	-	63±8	53±24
	6	-	-	-	-	-	57±15	46±3
	5	-	-	-	-	-	-	67±1
46.4	7	-	-	-	-		66±1	37±14
	6	-	-	-	-	-	53±14	67±1
	5	-	-	-	-	-	-	63±3
40.6	5	-	-	-	-	-	-	68±1 (196)

Table 3
Descriptive statistics of tensile strength test results.

	Quantity	Mean	Median	Minimum	Maximum	Std. Dev.	CV
Tensile strength	138	54,6	61,0	20,0	73,0	14,4	26%

method. The combination of two methods makes the algorithm characterised by relatively low computational complexity and allows the approximation of any function of several variables [33,34].

LMA is used for solution Nonlinear Least Squares Minimization problem which is given the following function (Eq. (1)):

$$s = \sum_{i=1}^{m} (y_i - f(\vec{x}, \vec{\alpha}))^2 \qquad (1)$$

where y is experimental measurements. Function $f(\vec{x}, \vec{\alpha})$ represents the value of the approximating function at the point $\vec{x} = \begin{bmatrix} x_1 \\ \cdots \\ x_n \end{bmatrix}$ (where n is number of variables) and $\vec{\alpha}$ is vector of coefficients of function. The step of the LM method is given by the formula (Eq. (2)):

$$z_{k+1} = z_k - [J^T J + \lambda I]^{-1} J^T \vec{e} \qquad (2)$$

where: $\vec{e}$ – vector of approximating error (Eq. (3)):

$$\vec{e} = \begin{bmatrix} e_1 \\ \cdots \\ e_m \end{bmatrix}, e_i = y_i - f(\vec{x_i}, \vec{\alpha}) \qquad (3)$$

J – Jacobian matrix (Eq. (4)):

$$J_{ij} = \frac{\partial e(\vec{x_i}, \vec{\alpha})}{\partial \alpha_j} \qquad (4)$$

λ – damping factor

In subsequent operations, z_{k+1} is calculated followed by the value of the matching error of the approximated function (s). If the error has increased, λ increases and returns to the calculation of z_{k+1}. In case the error has decreased, λ is reduced and goes to the next iteration.

The algorithm is commonly used to teach neural networks [35,36]. It is also used for modelling chemical and physical phenomena (e.g. in the creation of models: degradation of polymers [37], strength of materials [38]). For approximation, in this paper, gnuplot 5.0 was used.

3. Results and discussion

3.1. Effects of processing parameters on tensile strength

Table 2 presents the results from the tensile strength tests. Each number in the table represents the mean value of the tensile strength, together with the standard deviations reached from three samples.

Where there is a lack of the results, this indicates the inability to obtain completely filled samples that could be employed to determine tensile strength. The selected parameters caused a break in the moulding process because the force value limit of 9000 N (set to protect the machine) was exceeded. As can be seen from the 196 combinations of parameters settings, only 47 sets allowed the cavity to be completely filled and thus reached the next stage of the investigation. In total, 138 tensile strength test results were obtained. The obtained results are presented in the Fig. 6 and Table 2.

∗One fully-filled sample was obtained in a given combination of parameters
∗∗Two fully-filled samples were obtained in a given combination of parameters

For experiments in which no samples of the required shape were obtained, their tensile strength was assumed to be 0 MPa

The distribution of experimental data is not normal. In addition, they are characterised by a large spread. These indicates that the
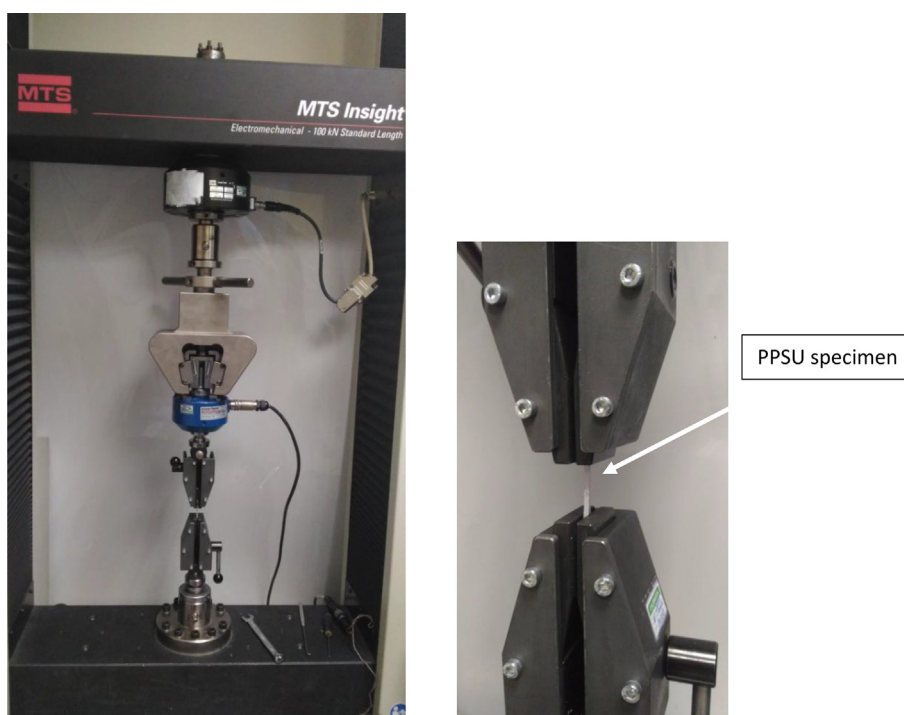
Fig. 5. Tensile machine used in the tests.

Fig. 6. Histogram of tensile strength test results.

	40,6	46,4	52,2	58	5	6	7	8	9	10	11	1,3	1,4	1,6	1,8	2	2,3	2,8
Quantity	3	15	33	87	15	21	20	21	24	16	21	3	6	9	12	24	39	45
Mean	68,0	57,3	62,4	50,7	54,3	49,2	48,6	52,5	59,5	54,1	63,1	65,7	55,8	54,8	58,8	56,6	52,2	53,6
Median	68,0	65,0	67,0	61,0	63,0	45,0	51,0	50,0	64,0	56,5	65,0	67,0	68,0	61,0	66,5	61,5	53,0	58,0
Minimum	67,0	21,0	26,0	20,0	25,0	27,0	20,0	23,0	35,0	29,0	38,0	61,0	29,0	35,0	33,0	30,0	20,0	21,0
Maximum	69,0	68,0	71,0	73,0	69,0	69,0	69,0	71,0	71,0	70,0	73,0	69,0	70,0	68,0	71,0	70,0	73,0	69,0
Std. Dev.	1,0	14,0	10,5	14,4	16,1	12,9	17,2	15,2	10,9	15,5	8,5	4,2	20,0	13,1	13,6	12,5	16,3	13,9
CV	1%	25%	17%	28%	30%	26%	35%	29%	18%	29%	14%	6%	36%	24%	23%	22%	31%	26%
Normal distribution	NO	NO	NO	NO	NO	YES	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO

Fig. 7. Histogram of tensile strength test results.

process is not stable in the tested parameter limits, and the result is affected by at least one of the input parameters of the process. Taking into account the variability of the data, the obtained results were divided into groups due to the values of individual parameters. The basic descriptive statistics were calculated and the normality of the distribution was examined (Fig. 7.)

The maximum number of samples was achieved from the highest amplitude value. Furthermore, when its value was decreased, the number of useable samples also decreased. This can be explained by the fact that the amplitude parameter has the greatest effect on the amount of ultrasonic energy conveyed to the pellets. The heat generated to melt a pellet is based on the square of the amplitude. Therefore, because the results are magnified by the square (rather than incrementally) small increases or decreases in amplitude have a greater effect. This is evidenced by the trials conducted where decreasing the amplitude value led more unfilled samples being produced regardless of the other parameter settings. This is because less energy lowers the heating rate of the polymer and so the plastification process has to be prolonged to melt the same volume of material. The ultrasonic exposure time parameter directly affected the duration of the ultrasonic vibration, whereas the plunger velocity parameter was responsible for the moulding force. Thus, when amplitude level is lower, complete filled specimens were produced only when the decreased values of plunger velocity were combined with an increased ultrasonic exposure time.

An amplitude of 40.6 μm is sufficient to melt the entire volume of the pellet only if it is combined with the lowest plunger velocity and the maximum ultrasonic exposure time.

Some of the results are characterised by high standard deviation, meaning that the process was not stable in terms of the mechanical property of the samples. This can be explained in the example shown in Fig. 8. Parts fabricated from this combination of parameters had dark marks on the surface, which points towards the overheating of the polymer. Visually, all three samples were degraded, but each in different locations. A significantly large disproportion of tensile strength values after the tests (1st 48 MPa, 2nd 44 MPa, 3rd 71 MPa) meant that a microscope was needed to see how the fracture surfaces on the samples looked. These observations confirmed that two of the specimens had similar signs of material degradation in the fracture section, while the fracture section in the third specimen appeared to be unaffected. Polymer degradation lowered the mechanical properties, but only if this occurred in the fracture region of the sample. In our study, we intentionally used brightly-coloured PPSU to visually control the external appearance of the processed parts, but it is important to be aware of this issue especially when processing dark-coloured PPSU.

On the other hand, parts that had a low standard deviation have none of the black marks on their surface that would indicate material degradation. Visual assessment did not find any significant differences between the three samples fabricated with each set of parameters.

Fig. 9 shows the changes in the tensile strength value of the PPSU specimens in function of the ultrasonic exposure time for different amplitude and velocity values. We can notice the same effect which was mentioned by Zeng et al. [22] – to the certain point of increasing the ultrasonic time, tensile strength is rising but then suddenly drop.

First, decreasing the amplitude level forces the plunger velocity to decrease, while extending the ultrasonic exposure time. For instance, for an amplitude of 52.2 μm, the maximum velocity was 9 mm/s, i.e. 2 mm/s lower than when using the maximum values of amplitude.
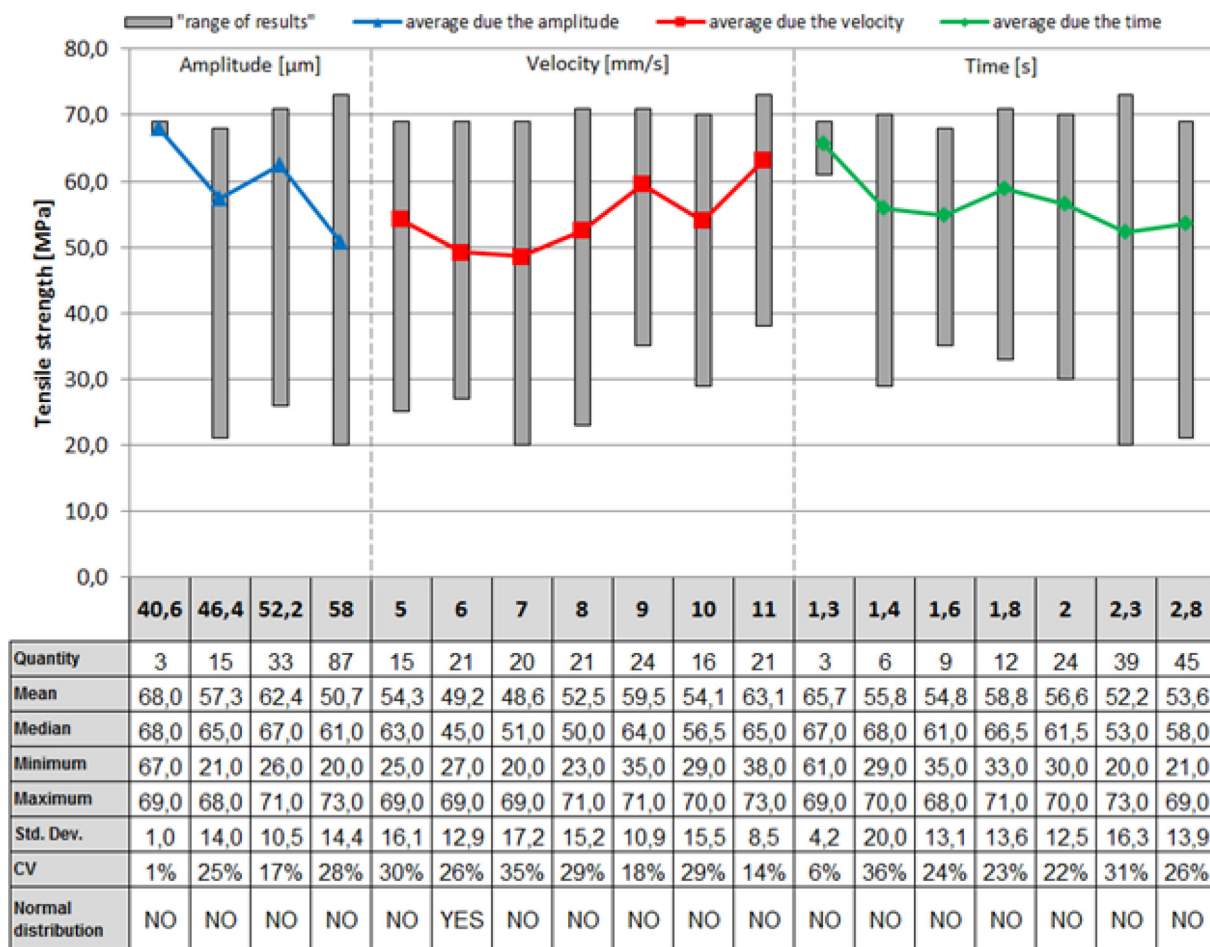
The amplitude parameter was responsible for the amount of heat that directly affects the other two parameters. Initially the PPSU pellets were heated up from the friction induced by the sonotrode until they started to melt. Then, ultrasonic cavitation took place and continued to melt the remaining volume of the pellet. As can be seen in the graph of dependence, especially when taking the combination of the maximum amplitude together with the low velocities into account, decreasing velocity values led to a decrease in the tensile strength. This is because the pressure decreased between the sonotrode and the plunger surfaces which, in turn, influenced cavitation. The cavitation effect is probably responsible for the thermal degradation of the molten material and lowering the properties of the polymer. The relationship between pressure and ultrasonic cavitation was reported by J. Bing-yan et al. [39].

Less ultrasonic energy requires extending the plastification and injection phase; phases which correspond to plunger velocity as well as ultrasonic exposure time. Each decrease in velocity involves an increase in ultrasonic time to overcome the distance between the start and finish position of the plunger.

Each amplitude value used in this study was appropriate to obtain samples characterised by high mechanical properties, but only when applied in combination with a specific value of the rest of the parameters. Here a mathematical model is also proposed, which includes all the interactions between the input parameters in order to predict tensile strength values.

3.2. Morphology of PPSU samples

Three sets of parameters were chosen to investigate the morphology of the surface. According to the previous statement that amplitude has the greatest influence on the PPSU properties, specimens with the highest and the lowest value of this parameter and the highest tensile strength were selected as well as samples with the lowest tensile strength and the biggest standard deviation. Into account were taken only this set of parameters where three fully-filled samples were
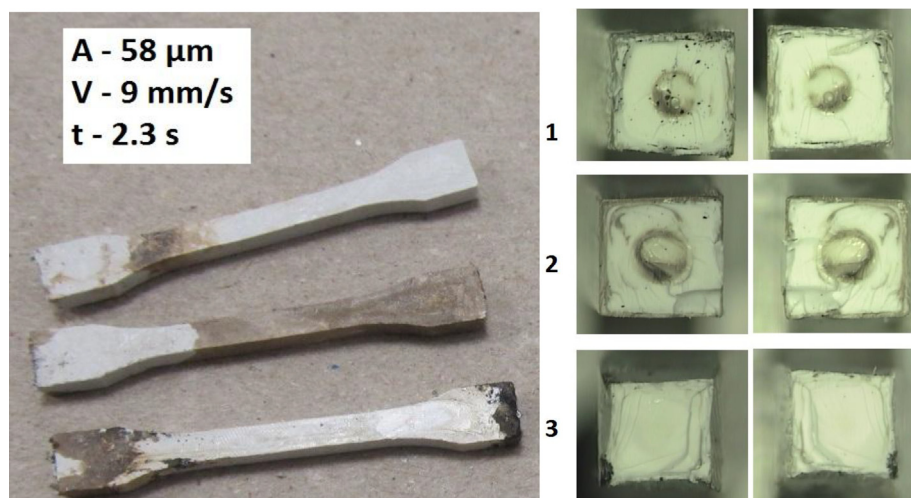

Fig. 8. Samples characterised by high standard deviation ($\sigma_M = 54 \pm 15$) and fracture surface at 40X.
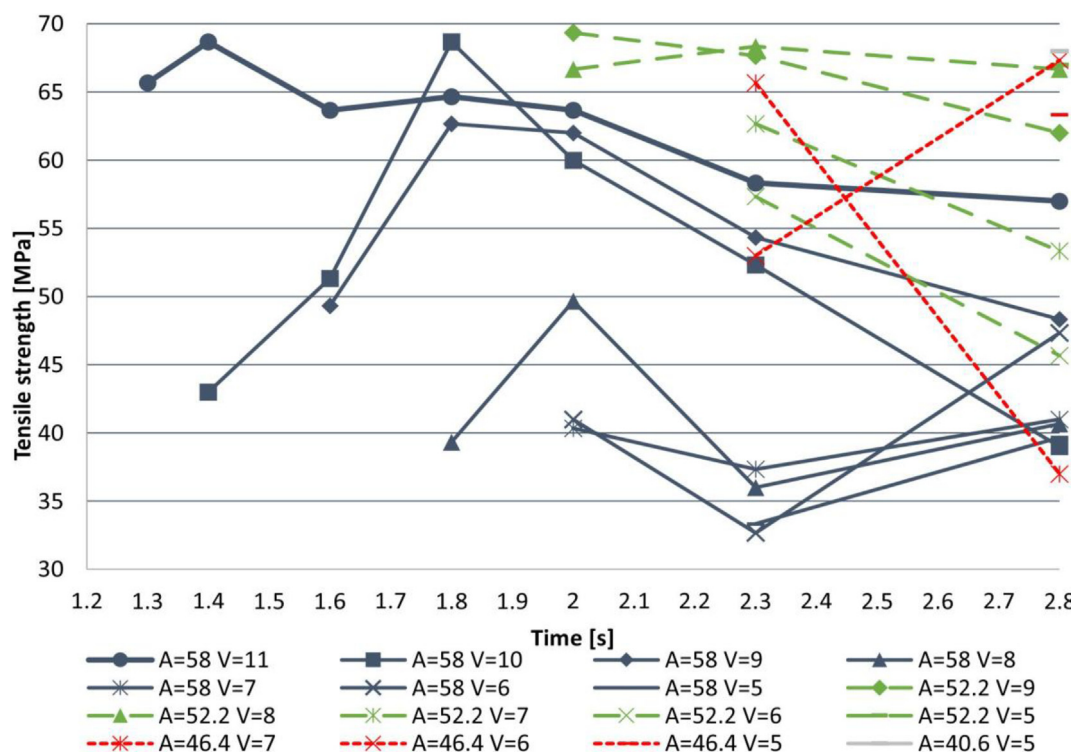
Fig. 9. Graph of dependence of input parameters on the tensile strength values.

obtained. Chosen specimens are highlighted in Table 2 – the numbers in brackets mean sample number.

Fig. 10 shows micrographs of selected samples, which before measurement were coated with 4 nm gold layer. Specimens with the highest tensile strength (a and c in Fig. 10) show absence of pores and also visually there were no dark marks. Highly degraded sample with very low tensile strength (b in Fig. 10) has on the surface numerous holes, which can be explained by cavitation process – exactly like in the Sacristán et al. [6] paper. Considering two sets of parameters but within the same amplitude value No. 2 and 48 respectively (a and c in Fig. 10) it can be seen how the ultrasonic micro-moulding process parameters influence on the morphology's sample. Velocity of 11 mm/s and the ultrasonic time of 1.4 s in the first set characterised the process by high pressure inside the chamber, what led to decrease air gaps between granules causing the medium more homogenous to distribute the energy. In the other set of parameters, mainly low velocity of 5 mm/s and long ultrasonic exposure time caused the high degradation of material what can be seen on the sample in Fig. 10b). Using these parameters the pressure in the chamber was low. When pressures inside the medium is low the bubble are under less resistance and became bigger what makes the ultrasonic cavitation effect more intensive. Thus, combining with the long exposure time of vibration the material was overheated.

3.3. Effects of ultrasonic vibration on chemical characteristics of PPSU

The specimens highlighted in Table 2 were also analysed by FTIR-ATR to check the degradation of PPSU, which occurs not only by chain scission, but also by aromatic ring broke and even carbonization which is visually visible at highly degraded samples. Three different sections of specimens, processed with the chosen set of parameters, were investigated: the centre and two ends.

In Fig. 11 the peaks at 3100–3030 cm^{-1} correspond to C−H aromatic ring stretch and 2960–2840 cm^{-1} to aliphatic C−H stretch. As it is typical, peaks above 3000 cm^{-1} are weak-to-moderate bands with comparison to the aliphatic ones. Aromatic C−H stretching is usually supported with the presence of the aromatic ring bands C═C−C at

1600–1450 cm^{-1}. Aromatic ring has also C−H in plane and out-of-plane bending vibrations which respectively occurs at 1230–1095 cm^{-1} and 870–815 cm^{-1}. It is also possible to observe signals at 1320–1290 cm^{-1} due to S(═O)$_2$ stretching [40,41].

Results show that high temperature and pressure are enough to degrade the PPSU through breaking the aromatic rings which is visible by C−H aliphatic bands presence near below 3000 cm^{-1} (Fig. 11). Results also indicate that the probability of degradation occurring is more likely in samples exposed for long sonication time. In combination of parameters No. 2 only one region indicates degradation (one end of sample). In order to exclude any mistakes, the additional analyse was performed (hence in Fig. 11a there are four spectra). Even though, all samples present in the paper have signs of degradation, the probability is less in this one, where the amplitude and velocity have the highest value but time of sonication is one of the lowest. This does not meet the statement of Grabalosa et al. [26] who report that parts processed with lower ultrasonic time tend to have more defects. It indicates that irradiation time should be longer for degradation resistant polymers to obtain more homogenous parts, but should be shorter for polymers which are more sensitive, to prevent their damage. Both PPSU samples in our study with long vibration time (No. 48 and 196) indicate the occurrence of degradation compounds, but the most interesting is the second specimen, which have high tensile strength – degradation is visible at FTIR spectra, but not in SEM micrographs. This means that some set of parameters start the degradation process, which does not go so far to affect mechanical and visual properties. Moreover, in this study no trend was observed between the different regions of the measured samples.

Thermal analysis was also performed. Used PPSU polymer is amorphous, which is shown on DSC thermograms, were only glass transition temperature (Tg) can be determined. Obtained Tg values (Fig. 12) are similar to each other: 217,1 °C (No. 2), 217,2 °C (No. 48) and 216,2 °C (No. 196), but much more interesting is a presence of effect known as 'Tg overshoot' in specimens from set of parameters number 48 and 196, where sonication times were one of the highest.

Amorphous polymers, which Tg is above room temperature are

a)

b)

c)
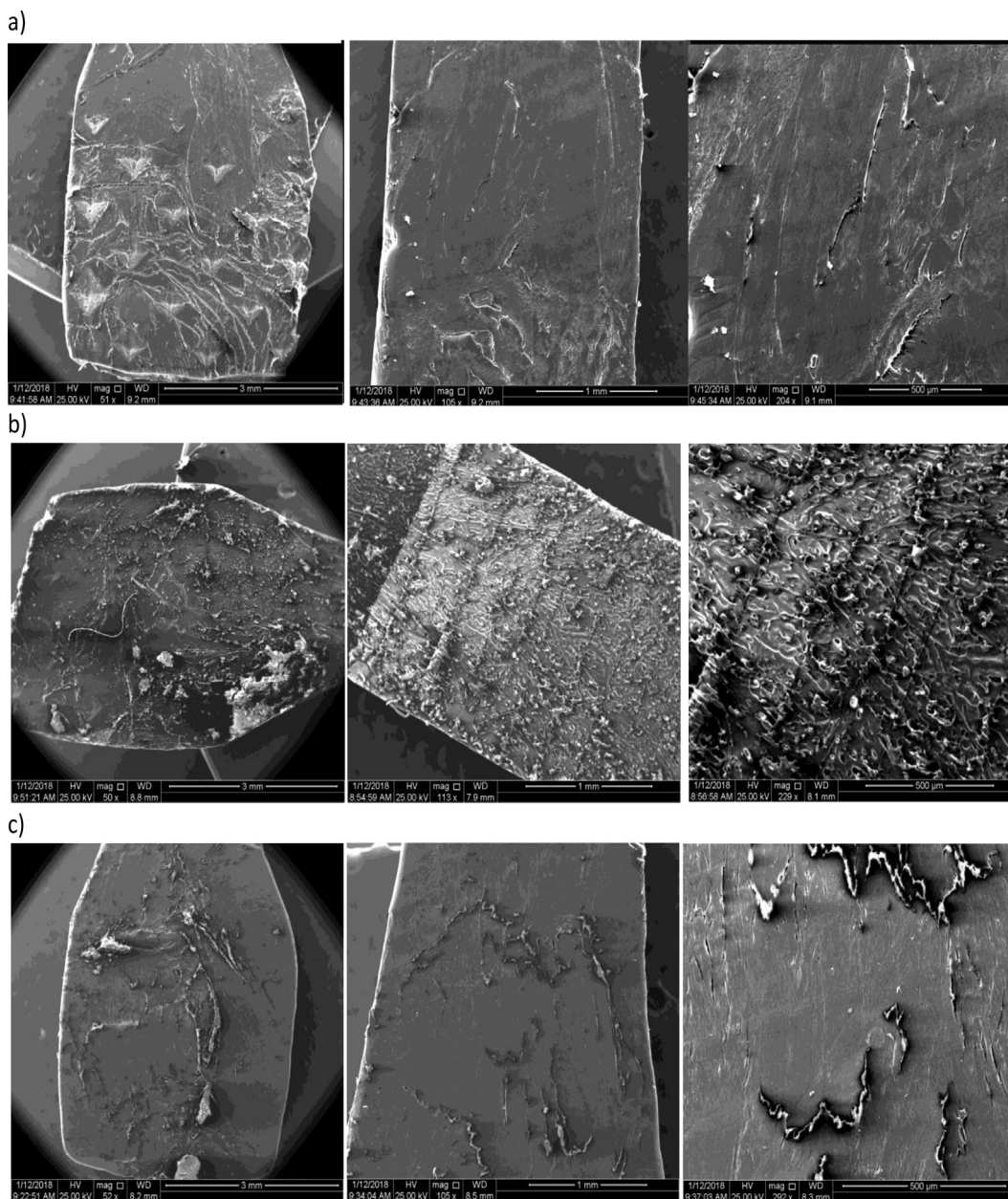
Fig. 10. SEM micrographs of specimens processed with combinations of parameters No. 2 (a), 48 (b) and 196 (c) in resolution 3 mm, 1 mm and 500 μm.

called as glassy polymers. In most cases they are not at equilibrium if they have undergone rapid cooling from the melt. Their molecules have not had sufficient time to relax to their optimum packing conformation, so during storage polymer chains slowly reorganize, which is called as 'physical ageing' or 'enthalpy relaxation'. The effect of aging is observed as an endothermic peak just above Tg.

More research should be done to check the repeatability of this effect in other samples, and to confirm the presence of some dependence between sonication time and susceptibility to physical aging [42].

3.4. Model of the mechanical strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process

To model the PPSU ultrasonic micro-moulding process, we used a function including the impact of individual parameters on the output and their interaction.

The general formula is (Eq. (5)):

$$y = \alpha_0 + \sum_{i=1}^{n} \alpha_i x_i + \sum_{i=1, j=2}^{n} \alpha_{ij} x_i x_j + \sum_{i=1}^{n} \alpha_{ii} x_i^2 + \alpha_{i,i+1,\dots,n} \prod_{i=1}^{n} x_i \pm \varepsilon$$

(5)

where:

α – coefficients of function
x – explanatory variables
ε – approximation error

Within the framework of the research, the experimental model has been developed to predict the tensile strength σ_M [MPa] of the PPSU specimens depending on three parameters: amplitude A [μm], plunger velocity V [mm/s] and ultrasonic exposure time [s]. Based on (eq. 1) with the assumption that x_1 = A, x_2 = V, x_3 = t and $y = \sigma_M$ we obtain (Eq. (6)):
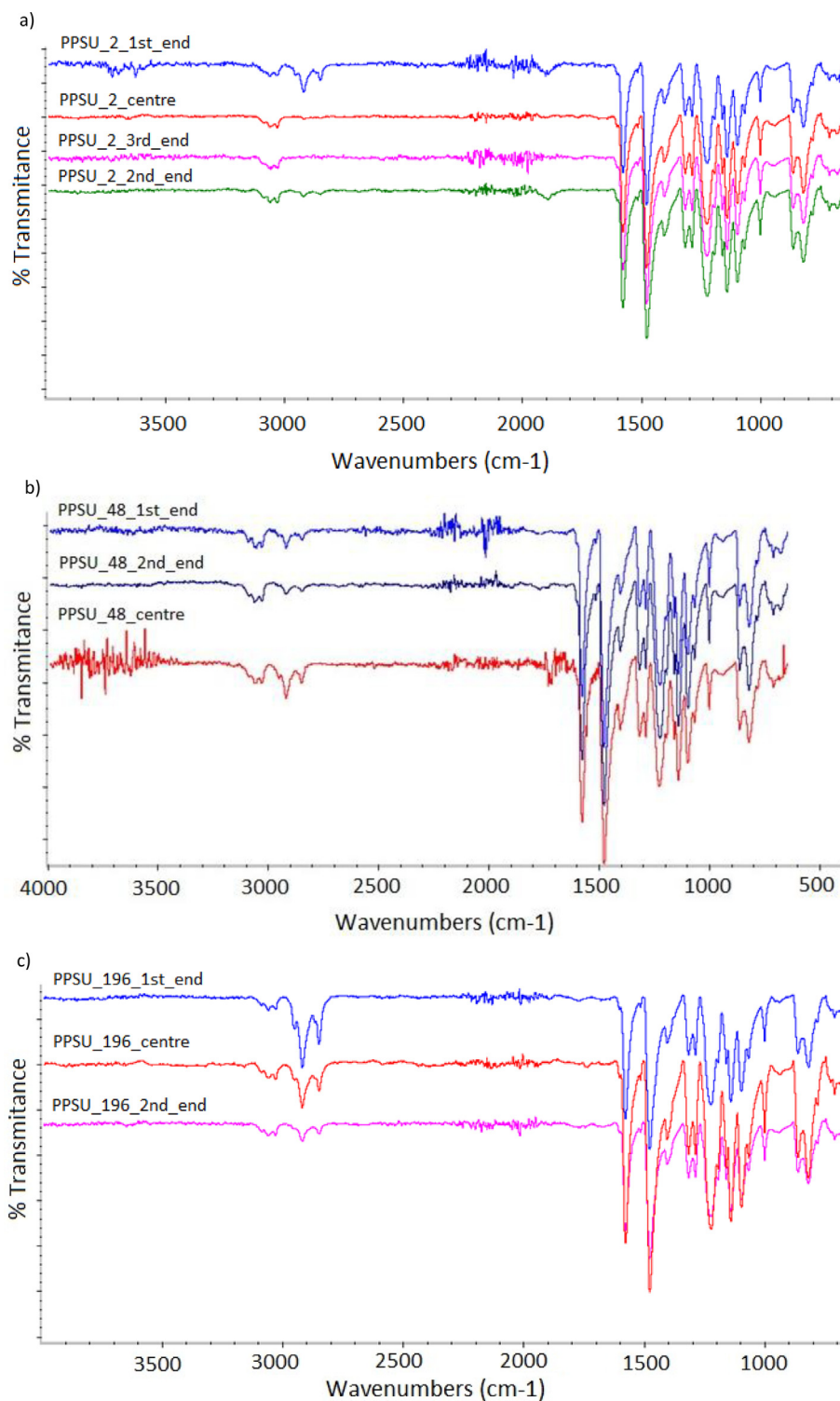
Fig. 11. FTIR ATR spectra of specimens processed with combinations of parameters No.: a) 2, b) 48 and c) 196.

$$\sigma_M = \alpha_0 + \alpha_1 A + \alpha_2 V + \alpha_3 t + \alpha_{12} AV + \alpha_{13} At + \alpha_{23} Vt + \alpha_{11} A^2 + \alpha_{22} V^2$$
$$+ +\alpha_{33} t^2 + \alpha_{123} AVt \pm \varepsilon \qquad (6)$$

To better fit the model, further calculations incorporated only those parameters that allowed completely filled samples to be obtained. The function field is as follows:
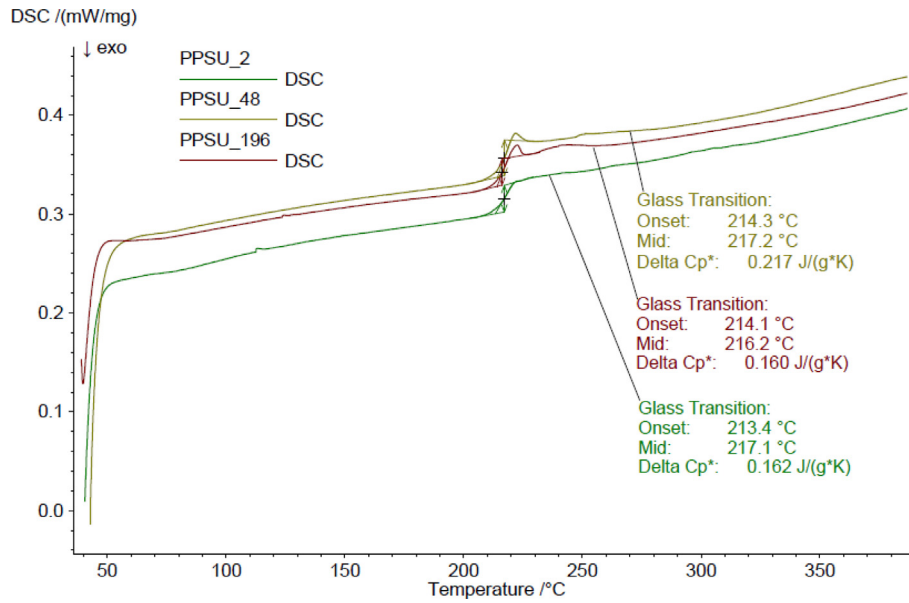
Fig. 12. DSC thermograms with Tg (glass transition temperature) determined.

$$for\ A = 58{,}0 \begin{cases} V \in (10;11] \rightarrow t \in [1.3;2.8] \\ V \in (9;10] \rightarrow t \in [1.4;2.8] \\ V \in (8;9] \rightarrow t \in [1.6;2.8] \\ V \in (7;8] \rightarrow t \in [1.8;2.8] \\ V \in (6;7] \rightarrow t \in [2.0;2.8] \\ V \in (5;6] \rightarrow t \in [2.0;2.8] \\ V = 5 \rightarrow t \in [2.3;2.8] \end{cases}$$

$$for\ A = 52{,}2 \begin{cases} V \in (8;9] \rightarrow t \in [2.0;2.8] \\ V \in (7;8] \rightarrow t \in [2.0;2.8] \\ V \in (6;7] \rightarrow t \in [2.3;2.8] \\ V \in (5;6] \rightarrow t \in [2.3;2.8] \\ V = 5 \rightarrow t = 2.8 \end{cases}$$

$$for\ A = 46{,}4 \begin{cases} V \in (6;7] \rightarrow t \in [2.3;2.8] \\ V \in (5;6] \rightarrow t \in [2.3;2.8] \\ V = 5 \rightarrow t = 2.8 \end{cases}$$

$$for\ A = 40{,}6 \{ V = 5 \rightarrow t = 2.8$$

Furthermore, taking into account the material specifications, the tensile strength value is:

$$\sigma_M \in (0;70)$$

As a satisfactory result of the experiment, we accept $\sigma_M \geqslant 65 MPa$.

This approach resulted from the fact that parts from these values were characterised not only by tensile strength values close to the material's specifications, but also because they have a low standard deviation that confirms to process stability.

The approximation of the function describing the ultrasonic micro-moulding process was carried out using the Marquadt-Levenberg algorithm. According to formulas (Eq. (1)) and (Eq. (4)), the function of the objective is (Eq. (7)):

$$s = \sum_{i=1}^{m} (y_i - (\alpha_0 + \alpha_1 A + \alpha_2 V + \alpha_3 t + \alpha_{12} AV + \alpha_{13} At + \alpha_{23} Vt + \alpha_{11} A^2$$
$$+ \alpha_{22} V^2 + \alpha_{33} t^2 + \alpha_{123} AVt))^2$$
$$\rightarrow min \tag{7}$$

And Jacobian matrix (Eq. (8)):

$$J = [-1, -A, -V, -t, -AV, -At, -Vt, -A^2, -V^2, -t^2, -AVt] \tag{8}$$

Using the gnuplot 5.0, the model coefficients for the Eq. (6) were estimated (Eq. (9)):

$$\sigma_M = -1655.3 + 39.8A + 162.0V + 549.8t - 2.7AV - 7.9At - 71.3Vt$$
$$+ -0.2A^2 + 0.4V^2 - 14.8t^2 - 1.17AVt \pm 7.9 \tag{9}$$

According to Table 4, it should be noted that there is a large correlation between the first eight coefficients. In connection with the obtained results, the approximations were again approximated, removing from the model successively one factor characterised by the greatest correlation with others ($\alpha 12, \alpha 13, \alpha 23$). The obtained models

Table 4
The correlation matrix between the various coefficients.

	α_0	α_1	α_2	α_3	α_{12}	α_{13}	α_{23}	α_{11}	α_{22}	α_{33}	α_{123}
α_0	1.00										
α_1	−0.96	1.00									
α_2	−0.92	0.80	1.00								
α_3	−0.98	0.88	0.95	1.00							
α_{12}	0.92	−0.81	−0.99	−0.95	1.00						
α_{13}	0.97	−0.90	−0.96	−0.98	0.97	1.00					
α_{23}	0.93	−0.84	−0.99	−0.96	0.98	0.97	1.00				
α_{11}	−0.93	0.85	0.98	0.95	−0.98	−0.97	−1.00	1.00			
α_{22}	0.34	−0.58	−0.03	−0.16	0.03	0.18	0.13	−0.14	1.00		
α_{33}	−0.01	0.06	−0.02	−0.01	−0.08	−0.04	0.02	0.01	0.03	1.00	
α_{123}	0.00	0.08	0.11	−0.07	−0.15	−0.10	−0.13	0.17	−0.02	0.10	1.00

Fig. 13. Approximation results: a) real tensile strength and approximate tensile strength and b) real tensile strength and relative approximation error.

were characterised by a model error greater than the initial one by about 10%. In connection with the above, the model that best explained the process described in this article was considered (Eq. (6)).

According to the charts in Fig. 13, the relative approximation error is within the range of 0 to 50%. The biggest differences between real tensile strength and approximate tensile strength are noted with an experimental tensile strength of about 30 to 50 MPa. Above 50 MPa, the relative approximation error does not exceed 20%. Within the range 61–67 MPa, it reaches 10%.The model's determination coefficient R^2 is 75%, what considering the level of process stability, makes the result satisfactory.

4. Conclusions

Ultrasonic micro-moulding technology is suitable for processing micro parts of polyphenylsulfone (PPSU). The adjustable process parameters, such as amplitude, plunger velocities and ultrasonic exposure time values, were proposed and their influence on tensile strength examined.

Experiments show that PPSU parts can be produced from different process parameters, however the interactions between them must be taken into account. To find the optimum combination of the process parameters, the mathematical model was implemented. The function used to create a model incorporated the influence of all the parameters along with the relationship between them. The best fits at 61–67 MPa and the error of 7.9 MPa makes the model very useful to start processing PPSU polymer using ultrasonic micro-moulding technology.

Practical part of this paper clearly indicates that amplitude has the greatest influence on the process' success – more than 60% of planned samples were obtain using the highest amplitude value (58 μm). Furthermore, the lower amplitude is, the longer time must be taken to obtain the samples, which is shown in Table 2. Velocity parameter is more complicated – the lower velocity is taken, the lower pressure is created, which intensify cavitation effect. On the other side, the investigations confirmed that high velocity resulted in higher samples' mechanical strength, but when this parameter is too high, the cycle is broken and not filled samples are achieved.

SEM analysis show that mentioned cavitation bubbles are responsible for material degradation, which is visible in the form of holes on the surface of highly degraded sample. FTIR-ATR spectra indicate the occurrence of aromatic ring scission, since aliphatic C−H stretching bands were observed. Moreover, the probability of degradation rise

with sonication time increment and it occurs even if it is not visible visually and through mechanical measurement.

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Chapter 4. The effect of weld line on tensile strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding technology

Chapter 4 presents investigation of weld line formation during processing of PPSU in ultrasonic micro-moulding technology. The weld line phenomena was analysed and its influence on tensile strength was presented.

This study was presented in an article entitled: ***"The effect of weld line on tensile strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding technology"***, submitted to International journal of advanced manufacturing technology in June 2018.

The effect of weld line on tensile strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding technology.

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Abstract

Melting and processing polymers via ultrasonic vibration is now possible, but the weld line that results and the influence it may have on tensile strength has yet to be investigated. When producing products characterised by high mechanical strength, the parameters of the process should be considered in relation to the weld line on the parts. Here, four sets of process parameters (three using ultrasonic technology and one using the conventional process) were used to produce parts whose weld line strengths were then determined and compared. Amplitude values were found to significantly affect the V-notch size and consequently the strength of the samples. Samples from parameters where the amplitude was high (52.2 µm, 58 µm) were characterised by a strength similar to that reached with conventional injection-moulding technology. Moreover, the experiments showed that when using specific process parameters the weld line strength is characterised by values akin to those of pure samples. Finally, the investigation revealed that this novel technology is a potential alternative to micro-injection moulding of high requirement polymers such as PPSU.

Key words: ultrasonic micro-moulding; ultrasound technology; polyphenylsulfone; PPSU; amplitude; weld line.

1. INTRODUCTION

Ultrasonic micro-moulding technology that uses vibrations above 20 kHz to plasticize polymers is now available. The main advantage of the process contrary to the standard micro injection moulding is its potential to melt and inject the material needed for one cycle. Micro injection moulding technology as one of the most efficient process is dedicate especially for the large scale production. The weight of the micro parts often represents only a few percentage of the whole shot weight what can lead to material waste in a small scale production. Moreover, the polymer is plasticized from a thermal and mechanical heating supplied by a screw in a barrel and small dozes increase a risk of long residence time, which can cause degradation of the polymer in a barrel. In ultrasonic micro-moulding technology, where the material is processed by ultrasounds, there are no heaters so there are no residence time. Additionally, the molten polymer shows reduced viscosity, which allows the use of lower moulding pressures compared to the standard injection moulding processes. All these advantages put ultrasonic micro-moulding process as a real candidate for demanding fields like medicine and electronics where single micro parts made from expensive polymers are

sometimes needed. It is very important that applications made of plastics should characterised by the same properties regardless of the technology in which they were made. Thus, it is crucial to constantly compare ultrasonic micro-moulding technology to the standard micro injection-moulding that has been employed for decades.

The ability to plasticize polymeric materials using ultrasonic energy was first reported by W. Michaeli et al. in 2002. (Michaeli et al., 2002) when they used the new plastification system in a prototype of a micro injection-moulding machine (Spennemann, 2000). The initial version, where a small amount of material was plasticized in an electrically heated cylinder, was later replaced by plastification using ultrasonic energy. Their experiments showed the concept not only to be very efficient in terms of plastification time, but also the processed polyoxymethylene (POM) was characterised by a homogeneous structure. This achievement prompted many researchers to explore the topic further and, as such, a number of investigations where this innovative processing method is applied to different polymers have been carried out to date. Some researchers were interested in investigating the commodity and engineering of the polymers, while others focused on the medical grades. The process's parameters and the influence they have on selected properties of the polymeric parts made from polypropylene (PP) were investigated by W. Michaeli et al. (Michaeli et al., 2011), K. Zeng et al. (Zeng et al., 2014) and P. Negre et al. (Negre et al., 2015). Moreover, high density polyethylene (HDPE) were also processed using ultrasonic moulding by B.Y. Jiang et al. (Jiang et al., 2009), poly(methyl methacrylate) (PMMA) by W. Wu et al. (Wu et al., 2016) and ultra-high-molecular-weight polyethylene (UHMWPE) by X. Sánchez-Sánchez et al (Sánchez-Sánchez et al., 2017) . Medical grades of polymers such as polylactide (PLA), polybutylene succinate (PBS) and polyamide (PA12) were studied by M. Sacristán et al. (Sacristán et al., 2014), M. Planellas et al. (Planellas et al., 2014) and J. Grabalosa et al. (Grabalosa et al., 2016), respectively. Only one study, that by T. Dorf et al., concerns high performance polymers, namely PPSU (Dorf et al., 2018).

As the ultrasonic process has already been proved capable of manufacturing micro parts from different polymers, the next step should be directed towards investigating how the process influences the typical defects of the polymeric parts that conventional injection moulding produces. One such defect is the well-known weld line or knit line that reduces the mechanical properties of the final product as well as affecting its appearance. The weld line forms where two or more streams of material meet and combine together (Harper and John Wiley & Sons., 2006). The strength of the weld line area depends on whether the processing conditions are adequate and/or if the macromolecular chains diffuse through the original interface and provides the weld with a strength close to that of the pure material; otherwise the strength will drop dramatically.

Cheng-Hsien Wu et al., using the Taguchi method, found that four process variables i.e., melt temperature, mold temperature, injection speed, and packing pressure, have the greatest influence on the weld line strength of PP and HDPE polymers (Wu and Liang, 2005). Later on, Lei Xie et al. investigated the relationship between weld line strength and processing parameters in micro injection moulding of polypropylene parts. The results showed that the

mould temperature, followed by the melt temperature, most affected weld line strength. Additionally, V notch measurements showed that the size in the middle region of the specimen was larger and deeper than at the edge. Finally, a smaller V notch area leads to a stronger micro weld line (Xie and Ziegmann, 2009). Furthermore, these authors also indicated that the gate dimension coupled with processing conditions have a significant effect on the weld line strength of PP and HDPE parts (Xie and Ziegmann, 2010). Researchers not only focused on factors that affect the weld line strength, but also on those that reinforce it. Chang Lu et al. (Lu et al., 2006) investigated whether the presence of ultrasonic oscillation could enhance the weld line strength of polystyrene (PS) in a way that would improve molecular diffusion. For PS/HDPE blends, they indicated that the melt temperature is crucial to enhancing the strength of the weld line through ultrasonic oscillation. When the melt temperature is 230°C, ultrasonic oscillation can increase the weld line strength of the blends, which is contrary to when the melt temperature is 195°C. The advantage of using ultrasonic oscillation to reinforce weld line strength in micro injection moulding processes was also reported by Lei Xie et al. (Xie et al., 2010). They studied two ultrasonic inducing modes and their results showed that Mode 1 when the oscillation is induced from injecting to ejection moment produced better effects than Mode 2 did (the oscillation is induced from injecting moment to packaging finishing). For reasons of reinforcement, the weld line strength using ultrasonic oscillation they introduce is the curving weld line and the almost disappeared V-notch.

In this study, the authors subjected PPSU polymers to ultrasonic micro-moulding technology to investigate the resulting weld line strength. For the first time the weld line formed from this novel technology has been studied. Three different sets of ultrasonic process parameters were used to fabricate the complete filled samples and the best set from which it is possible to obtain the parts characterised by the highest tensile strength were introduced. Furthermore, the results from the best set were compared to those obtained from standard micro-injection moulding technology.

2. EXPERIMENTS

2.1. Material

The Radel® R-5100 GY1137 polyphenylsulfone used for this study is a commercially available material supplied by Solvay Ltd. PPSU is an amorphous material characterised by some outstanding properties; particularly its thermal (207°C) and chemical resistance. The material's general properties are shown in Table 1. Thanks to these features, the material is often used in the medical industry for a variety of applications such as nebulizers, humidifiers, flow controls, dental and surgical instruments, fluid containers, heart valve cases, microfiltration apparatus and other kinds of equipment (Platt, 2003; Sastri, 2014).

Table 1. General property of PPSU

Properties	Values
Density (g/cm3)	1.30
MFR (g/10 min)	17
Tensile stress (MPa)	70
Heat deflection temperature (°C)	207 (1.82 MPa, unannealed)
Thermal expansion coefficient (μm/m °C)	56
Glass transition temperature (°C)	220
Thermal conductivity [W/(m K)]	0.35
Dielectric strength (kV/mm)	14

2.2.   *Micro-moulding equipment*

The ultrasonic micro moulding machine Sonorus® 1G, developed by Ultrasion S.L., was used to manufacture the small specimens (complying with the EN ISO 527-2/1BB standard) (Fig.1) (www.ultrasion.com). The machine mainly consists of a bench, a mould system moved by skates and linear guides, an ultrasonic head and a feeding system that provides the pellets. The ultrasonic head converts the electrical waves, produced by an electronic ultrasonic generator generator (maximum power 1500 kW), into mechanical vibrating at an ultrasonic frequency of 30 kHz. This mechanical vibration is then transmitted to a sonotrode (Fig. 1). The material being processed begins to melt as it encounters the vibrating sonotrode (this is due to the thermal energy or (latent) heat of fusion, which occurs because of ultrasonic wave absorption and the frictional movement between the surfaces). Next, the melt is pushed by a plunger (maximum available force equal 6000 N) through the channel to the cavity where it is solidified and finally ejected (Fig.2). The adjustable process parameters are: amplitude (μm), force (N) and ultrasonic exposure time (s). It is important to mention that the machine has 9 available levels of amplitude values. The maximum value of 58 μm equals 100%. The amplitude can gradually be decreased in increments of 10 percent, e.g. 90% - 52.2 μm, 80% - 46.4 μm, and so on. It can be explain by the fact that, the mechanical amplitude is provided by the ultrasonic transducer at full power. Then, the amplitude value can amplify or reduce by means of mechanical elements, such as booster and the sonotrode, what is related to its geometry. For example the standard stepped sonotrode of the Sonorus 1G has an approximate gain of 6.25. On the other hand, the machine allows to limit the voltage given to the converter in steps of 10%, which will limit its output amplitude.

The temperature of the mould is a key factor as this determines the quality of the finished PPSU part. Mould temperature affects not only the shrinkage and warpage of the part, but also the level of moulded-in stresses (Solvay Specialty Polymers, 2015). To fulfil the supplier-recommended temperature of 138-163°C, the aluminium mould was built and equipped with an oil circulation flow. As the PPSU polymer must be dried to avoid cosmetic defects, a standard dryer for injection moulding machines was used.

Dosing

Ultrasonic head

PPSU specimen

Sonotrode

Movable plate

Mould

Fixed plate
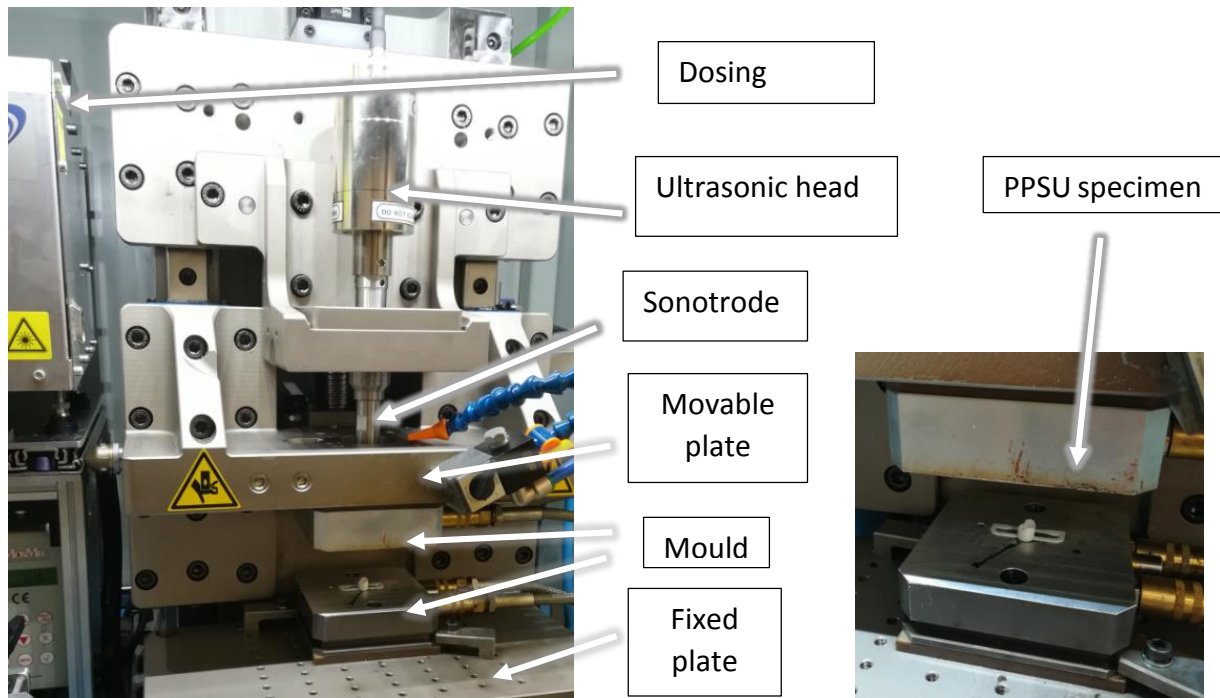
Fig.1. Experimental setup: a) Sonorus® 1G moulding machine, b) mould

Ultrasonic Generator

Converter

Booster

Sonotrode

Plunger is moving up with a force

Granules are melting and filling the cavity

Melt is filling the cavity
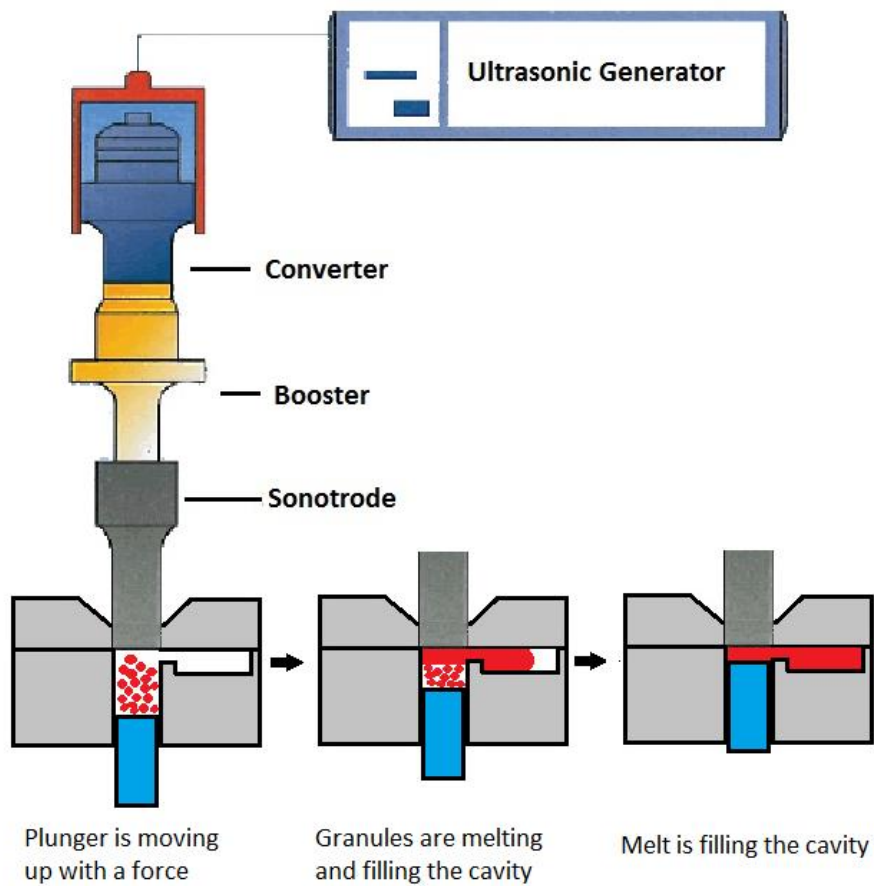
Fig.2. Scheme of the ultrasonic micro-moulding process

2.3. Process parameter settings and sample manufacturing

The experiments were conducted to examine how a set of ultrasonic micro-moulding parameters influenced the weld line strength of the PPSU samples. Earlier, T. Dorf et al., conducted extensive experiments with different process parameters and analysed their impact on the tensile strength of the PPSU specimens. The mathematical model describing the process was presented. The study confirmed that amplitude is the most influential parameter during the processing of the PPSU polymer (Dorf et al., 2018). That is way amplitude variable was selected as the main process parameter and its levels were modified. The applied process parameters resulted from technological trials, which were performed as screening experiments. The experiments were carried out to avoid the situation where a decrease in strength could have been caused by the degradation of the polymer. Thus, the acceptable processing parameters were characterised by the ability to obtain completely filled samples without visible signs of degradation. These experiments allowed the minimum amplitude level of 46.4 µm, which is capable to melt the PPSU polymer, to be firstly determined. Middle amplitude value correspond to the magnification of 10%, whilst the value of 58 µm is a maximum value available in the machine. Then, for three amplitude levels the ultrasonic exposure time was adopted in such a way that ultrasonic exposure did not degrade the samples. This provided three different sets of process parameters (see the values in Table 2). The force was constant. From each set of processing parameters in Table 2, 15 specimen pieces were manufactured for further analysis.

In addition, the 15 specimen pieces (Fig. 3b) with weld lines for comparative purpose were manufactured from an Arburg Allrounder 350 injection moulding machine equipped with a micro-injection moulding module (see parameters in Table 3). According to the supplier's recommendations, the PPSU granulates were dried at 149 ^{o}C for 2.5 h prior to the experiments.

Table 2. Processing parameter values for ultrasonic micro-moulding

Parameters	Unit	Values		
		1	2	3
Amplitude	µm	46.4	52.2	58
Ultrasonic exposure time	s	5.5	4.8	4
Force	N		2000	
Mould temperature	^{o}C		145	
Frequency	kHz		30	
Cycle time	s		20	

a)   b)
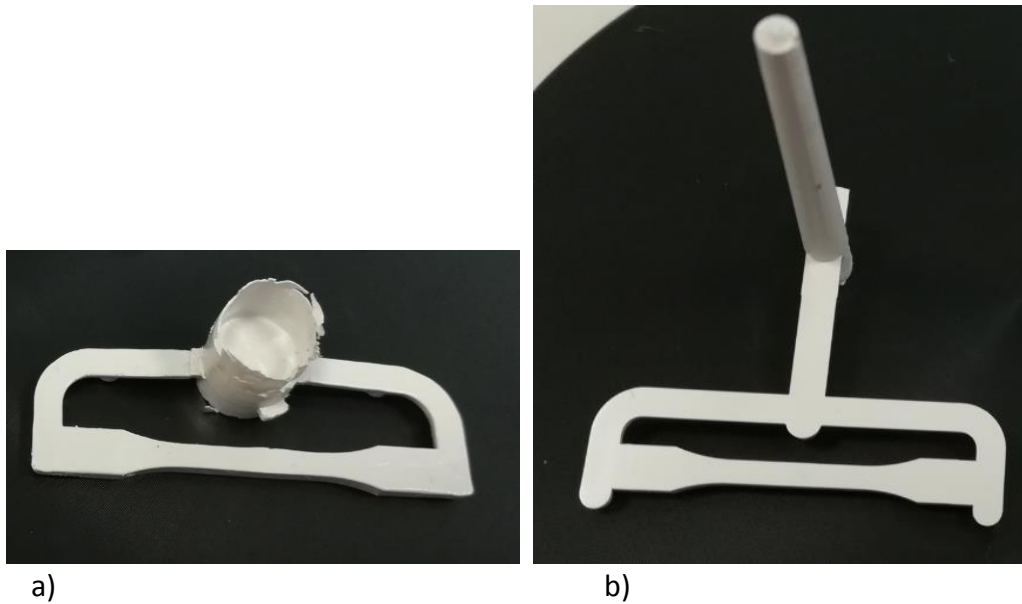
Fig.3. Mouldings from: a) ultrasonic micro-moulding process vs b) micro-injection moulding
process

Table 3. Processing parameter values for micro-injection moulding

Parameters	Unit	Values
Injection pressure	bar	1000
Injection time	s	1
Packing pressure	bar	1000
Packing time	s	3
Mould temperature	°C	145
Melt temperature (nozzle)	°C	375
Cycle time	s	25

2.4.   Measurements

The manufactured specimens (60 parts, 15 from each set of parameters) were tested for tensile strength σ_M using the MTS Insight 100 kN machine. Tests were performed in compliance with the EN ISO 527-2 standard at a test speed of 5mm/s and a data equation rate of 25 Hz. In order to present the results, statistical computations were carried out using the Minitab version 17 software.

Moreover, the morphology of the three samples from each set of parameters fabricated by ultrasonic micro-moulding technology, together with the one sample from conventional micro-injection moulding technology, were inspected by the scanning electron microscopy Quanta 650 FEG from FEI Company. The areas of measurement are present in Fig. 3. Each

specimen was cut off across the weld line. Then, the sample was prepared by mounting one piece in the resin and polishing it. Due to the low electrical conductivity of the sample, the test was carried out in a low vacuum mode and the mounted samples were coated with 15nm of carbon to remove the electric charge from the surface of the sample. The images were recorded using a backscattered electron detector (BSE-vCD), which provided a material contrast. Each unmounted sample was imaged at x100, x1000, x4000 and x5000.

Fig.4. Dimensions of manufactured specimen (unit: mm) and scheme of SEM areas of weld line

3. RESULTS AND DISCUSSION

3.1. *Tensile strength*

Preliminary tests carried out in order to select parameter values to obtain completely filled samples without visual signs of degradation allow to observe the relation between amplitude and ultrasonic exposure time shown in Figure 5. As can be notice decrease amplitude cause increase the ultrasonic duration time. Amplitude directly affect on the melting phase in the way that the heat generated to the melt is based on the square of amplitude. Thus small modification in amplitude value have a great effect on the plastification process, mainly on the duration of it. Interaction between process parameters on tensile strength of PPSU samples in a wider range is described in the work done by T.Dorf et al. (Dorf et al., 2018).

Fig.5. Relation between amplitude and time

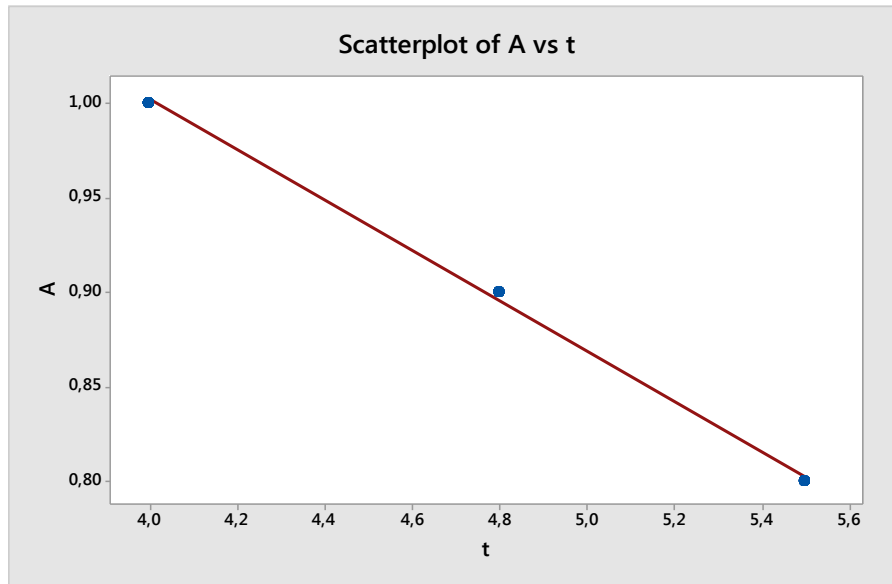Table 4 and Figure 6 depict the results from the tensile strength tests of the three sets of ultrasonic micro-moulding technology (US) and that of the conventional injection micro-moulding technology (IM). The weld line strength from the first set of parameters has the lowest values (63.27 MPa) and the highest standard deviations. Weld line strength increased with increasing amplitude level, something which is reflected by the average values of 69.47 and 69.53 MPa, respectively. The highest tensile value and lowest standard deviations were observed in the samples from the conventional injection-moulding technology. As can be seen the micro-injection process is more stable than ultrasonic micro moulding but it must be taken into consideration that, the ultrasonic process is less known contrary to injection moulding. Lower average tensile strength may result from the signs of degradation inside the some of the samples, which influenced the overall result. Both the ultrasonic and conventional processes are able to obtain weld line samples with strengths similar to the samples without weld lines (70 MPa according to supplier specifications).

Table 4. Average tensile strength values and dispersion

Technology	Set No.	Average tensile Strength [MPa]	Standard deviation (s)	Variance (s²)	Mean absolute deviation (MAD)
Ultrasonic micro-moulding (US)	1	63.27	8.03	64.63	6.41
	2	69.47	1.80	3.26	1.44
	3	69.53	2.23	4.98	1.89
Injection micro-moulding (IM)	4	71.27	0.45	0.20	0.39
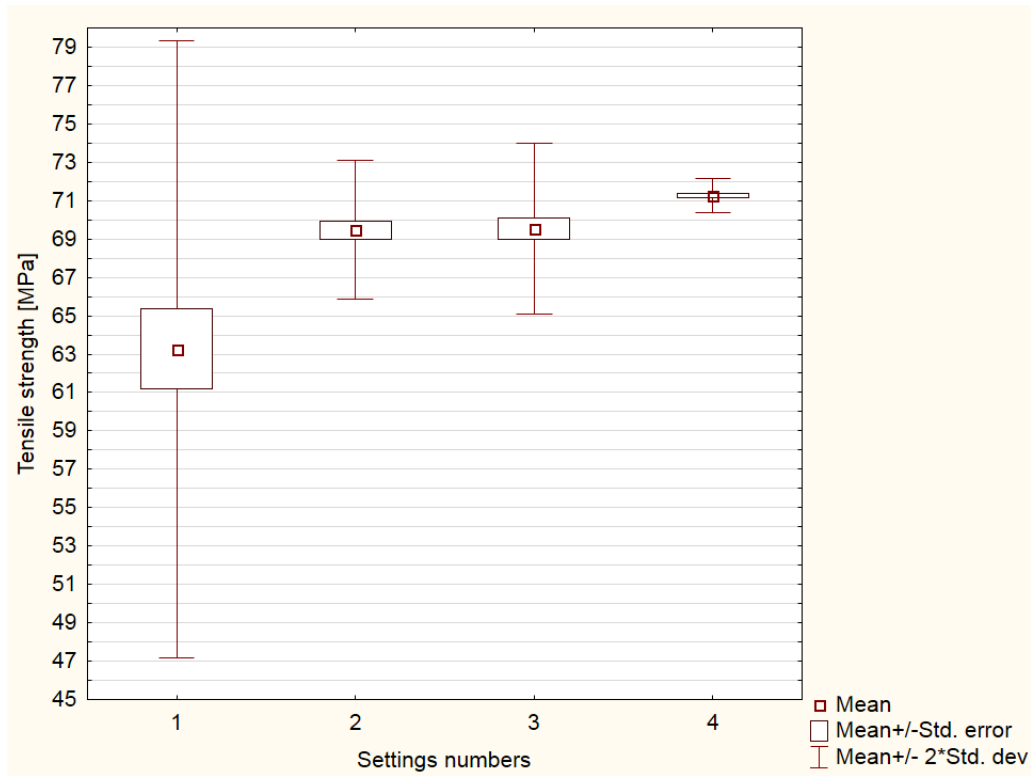
Fig.6. Comparison of samples from different sets of parameters and technologies

Tensile strength value, as the most important and measurable characteristic, was compared to find any differences. A histogram of results is shown in Figure 7. As seen on the histogram, the second and third sets of parameters from the US processes produced parts which have a similar average tensile strength and dispersion, whereas the specimens from the first set of parameters are characterised by the lowest strength values and have with the highest dispersions among the results. The specimens with the highest tensile strengths and lowest dispersions came from conventional injection moulding technology.
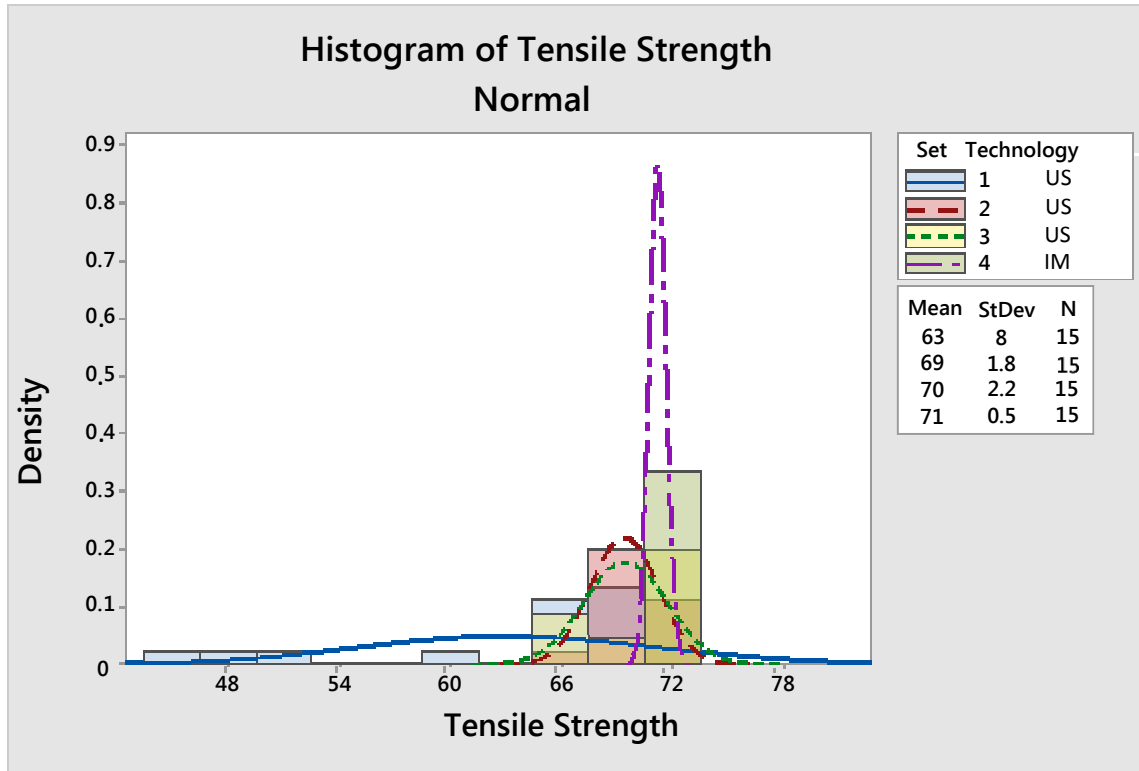
Fig.7. Histogram of tensile strength

In terms of sample dimensions, the Ryan-Joiner normality test was performed to assess the normality distribution of the tensile strength (Ryan and Joiner, 1976). As seen in Figure 8, set no. 1 is not characterised by normal distribution (p-value < 0.01), whereas the results for sets nos. 2, 3 and 4 indicate distribution close to the normal (both p-values > 0.1). The lack of normal distribution in set no. 1 indicates that the process is not stable.
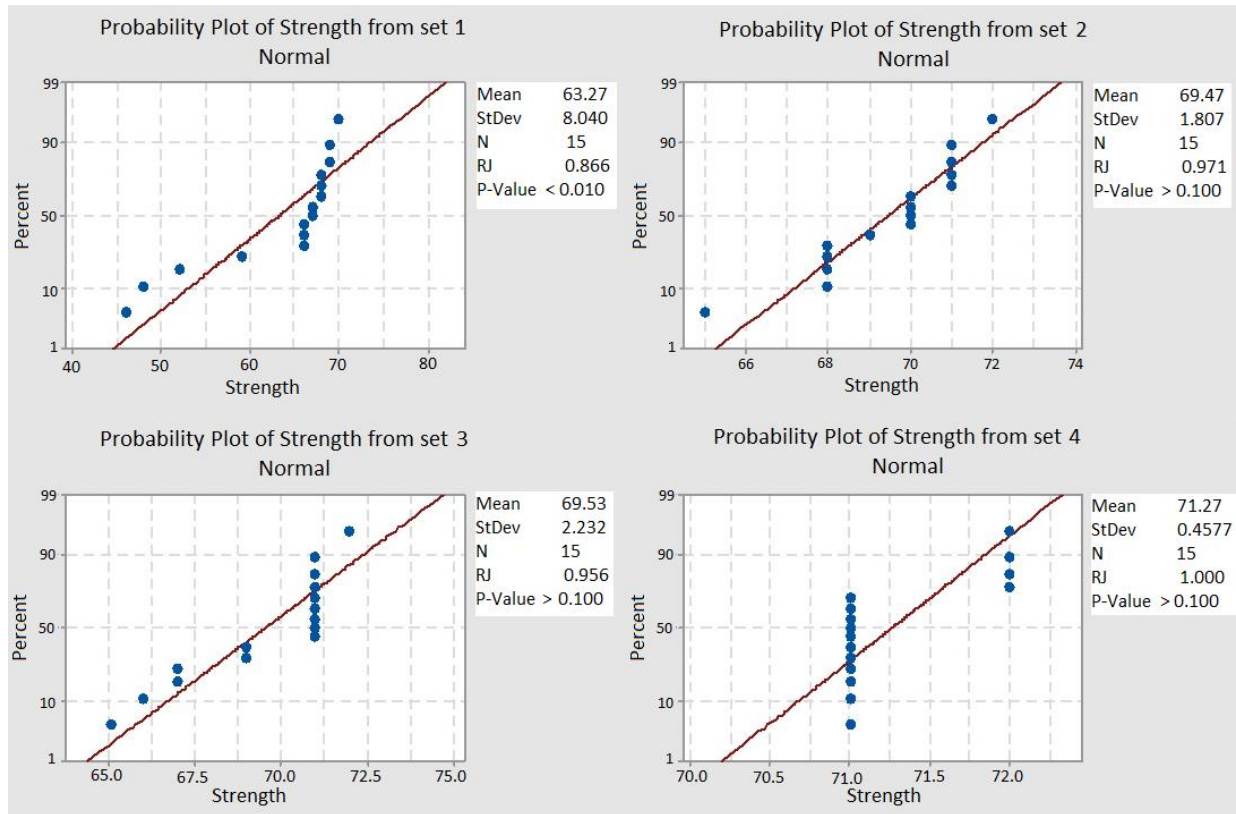
Fig.8. Probability plot of samples strength

To verify the hypothesis of variance equality, the Levene's test was performed (Levene, 1961). Results from the test (Figure 9) proved that the variations are different. Using the first set of parameters, namely the lowest amplitude value together with the longest ultrasonic time duration, not only does the lowest mean tensile strength disqualify this parameter setting, but so too does the high level of variations. Higher amplitude levels, 52.2 µm and 58, respectively, cause a decrease the variances. The smallest variability is characterised by the conventional injection micro-moulding process.
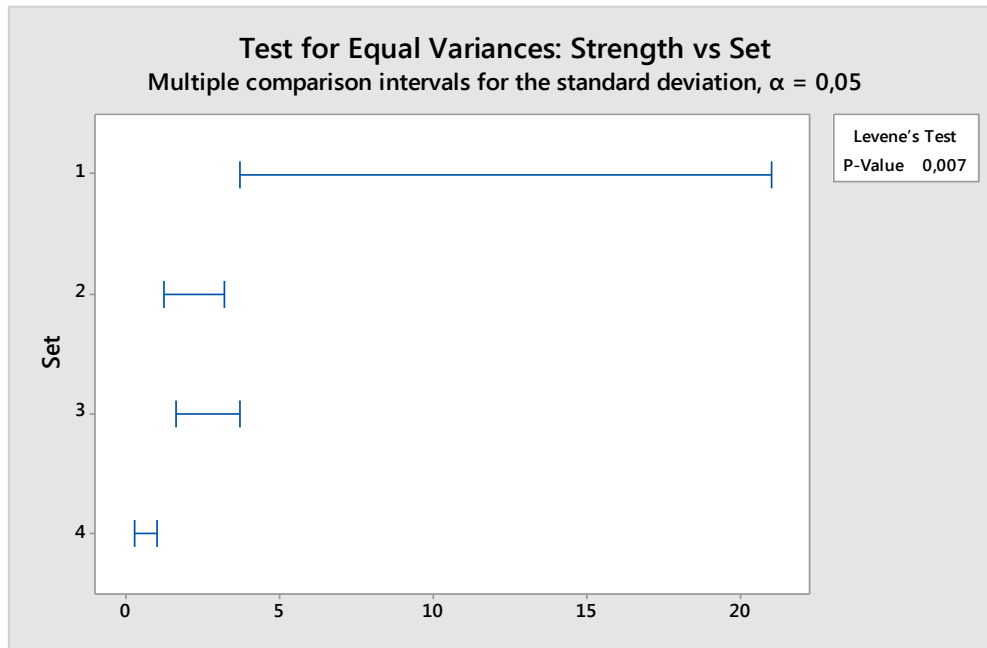
Fig.9. Test for equal Variances: Tensile strength vs Strength

3.2.   *Morphology*

The weld lines produced in PPSU specimens were determined. According to the literature, the V-notch has a significant influence on the weld line properties because by decreasing the V-notch, the strength of weld line is increased (Lu et al., 2006; Wang Cuntao, Uawongsuwan Putinun. Yang, Yuqiu. Hamada, 2007; Wu and Liang, 2005; Xie et al., 2010; Yu et al., 2006). In this paper, the V-notch appeared in each of the processing parameter settings and its impact on the tensile values obtained was examined. In the form of width and depth, Figure 10 shows the weld lines present on the specimen before being cut (left side) after being cut off (as explained in Figure 4), and after polishing (right side). In analysing the specimens from the ultrasonic micro-moulding process (sets 1, 2 and 3), it can be seen that the biggest V-notch depth (422.5 µm), which is characterised by the lowest average tensile strength of 63 MPa, is observed in the first set of ultrasonic parameters. Increasing the amplitude level firstly to 52.2 µm and then to 58 µm, caused a decrease in the V-notch depth to 4.6 µm and 2.8 µm, respectively, which led to the improved mechanical properties of the samples. It can be also noticed that such as small changes of V-notch depth between the 2nd and 3rd parameters settings does not influence on tensile strength values and there are resulting in comparable values. This may be explained by referring to the experiments performed by W. Wu et al. (Wu et al., 2016). They reported that amplitude level has a significant impact on the interfacial friction phenomenon and their results showed that the average heating rate increased from 460.4 to 1687.5°C/s as the amplitude increased from 10 to 30 µm. Moreover, PMMA granulates were plasticized from 30 to 160°C. The higher amplitude level is, the greater the ultrasonic plasticized rate is. Hence, the amplitude level in the ultrasonic micro-moulding process directly affects the melting temperature and it is well-known from the conventional injection moulding process, that higher temperature values decrease the size of the v-notch.

Experiments also showed that V-notch width does not influence the weld line strength. This is similar to the conclusion drawn by E. Debondue et al. (Debondue et al., 2004). The smallest V-notch was observed in the samples fabricated using the conventional micro-moulding technology.
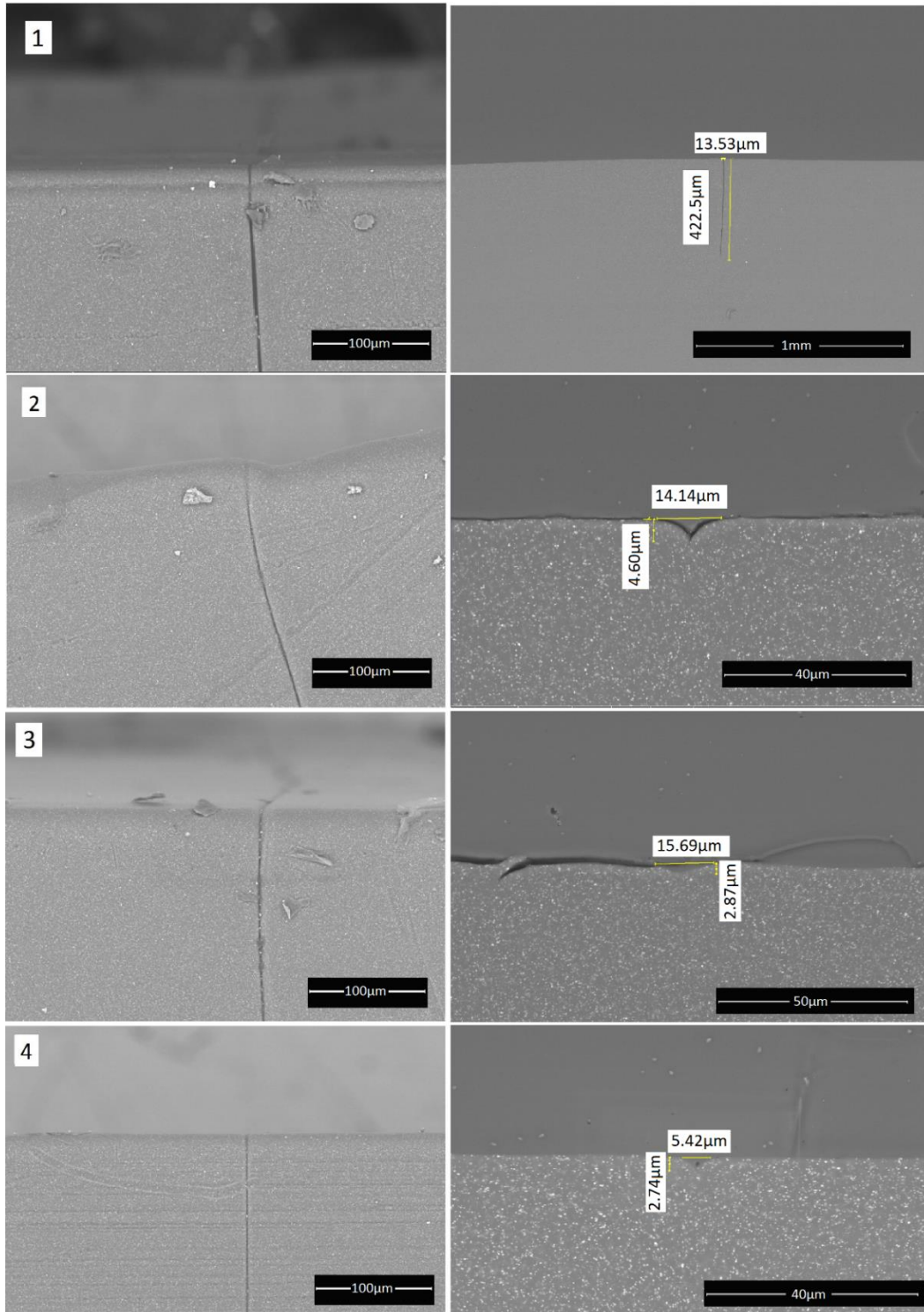

Fig.10. SEM micrographs of weld line from ultrasonic micro-moulding (1,2,3) and injection micro-moulding (4) processes

4. CONCLUSIONS

The effect weld lines have on the tensile strength of polyphenylsulfone in ultrasonic micro-moulding technology was investigated. Three different amplitude levels and ultrasonic exposure times were used to fabricate samples from which tensile strength values were then determined and compared to the tensile values of the samples made using a conventional injection-moulding process. The experiments conducted allows the following conclusions to be drawn:

1. Both in ultrasonic and conventional processes using appropriate parameters the presence of weld line do not reduce tensile strength of the samples. Similar values for PPSU samples without weld lines were reported by T. Dorf et al. (Dorf et al., 2018).
2. Weld line strength from the second and third sets of parameters for the ultrasonic micro-moulding technology is similar to that from conventional injection micro-moulding technology, but the process is more unstable.
3. The depth of V-notch directly affects the strength of the weld line in such a way that its magnification reduces the properties of the weld line.
4. Amplitude levels directly affect the formation of the weld line. The higher its value is, the greater the weld line strength.

Performed experiments gives the knowledge of the weld line formation in ultrasonic micro-moulding process. Results proved the ability to utilize the ultrasound to produce micro parts from PPSU as an alternative method to micro injection moulding technology overcoming all limitations resulting from standard technology in case of low volume production. Features, such as low energy consumption, material savings, low moulding pressures will definitely lower the production costs and allow the products of high performance applications to be more affordable.

5. ACKNOWLEDGEMENTS

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Chapter 5. Characterizing Ultrasonic Micro-moulding Process of Polyetheretherketone (PEEK)

Chapter 5 introduces the successful processing of polyetheretherketone in ultrasonic micro-moulding technology. Analyses the influence of main process parameters on the mechanical and chemical characteristic.

This study was presented in an article entitled: *"Characterizing Ultrasonic Micro-moulding Process of Polyetheretherketone (PEEK)"*, published by International Polymer Processing in August 2018 (Dorf et al., 2018).

Dorf, T., Ferrer, I., Ciurana, J. (2018). Characterizing ultrasonic micro-moulding process of polyetheretherketone (PEEK). International Polymer Processing, 33, 442-452.

Abstract

Ultrasonic micro-molding technology can dispense, melt and inject as small an amount of polymer as is required for one cycle, an advantage which makes the process highly desirable for low-volume and customized production of micro parts made from sensitive and very expensive polymers, especially in the medical sector. In this study, the feasibility of processing the polyetheretherketone (PEEK) polymer was investigated. The experiments conducted determined the parameters of a process that would allow parts with specific mechanical properties to be produced and verified as not degraded. The development of the process used three amplitude values as well as varying plunger velocity and vibration times. The three amplitude values and four speed values were tested to determine appropriate parameters for the ultrasonic process. Completely filled samples without any visual signs of degradation were analysed using FTIR-ATR, crystallinity percentage and tensile strength tests. Results show that the amplitude parameter is an important factor in the ultrasonic process and the higher its value is, the better the mechanical properties of complete parts are. Moreover, the tensile strength value of the specimens fabricated by ultrasonic micro-molding is comparable to that of conventional injection molding technology.

Chapter 6. Results and Discussion

Chapter 6 summarizes the results of the Thesis and the related discussion.

6.1. Ultrasonic micro-moulding of PPSU

Trials in which 196 combinations of parameters settings were used were carried out in order to analyse the impact of the main ultrasonic micro-moulding parameters (amplitude, plunger velocity and ultrasonic exposure time) on the mechanical and chemical characteristic of polyphenylsulfone. Only 47 sets allowed to produce the well-shaped samples suitable for the further stage of the research. Furthermore, the majority of the samples were fabricated using the maximum amplitude value of 58 µm, proving that its value is the most influential among others. The heat generated to melt polymeric materials is based on the square of the amplitude, thus small increase or decrease of its value have a greater effect. This was confirmed by the results, where decreasing amplitude value caused the production of defective (not filled) samples regardless of the other parameter settings. Less energy lowers the heating rate of the polymer, thus only extending the plastification process allows to melt the same material volume, giving completely filled samples. Presented results reveal that each amplitude value used in the experiments is appropriate to obtain samples with high mechanical properties but only combined with the specific values of the rest parameters. Included all of the interactions between the inputs parameters, the mathematical model is proposed. Its experimental error of 10% in the range of 61-67 MPa causes that it can be used to the preliminary selection of input process parameters in order to achieve high quality mouldings. This will definitely minimize costly technological trials and help to start processing PPSU polymer using this novel technology.

It should be emphasize, that this model is an insufficient tool to estimate nonlinear material behaviour in the ultrasonic micro-moulding process. For this purpose mathematical modelling should be consider in the terms of energy balance and thermodynamic laws. Up to date there are some work relay on modelling of ultrasonic plastification process. Given that three heating effects are responsible for melting the polymer, namely interfacial friction, viscoelastic heating and cavitation, only the analysis of PPSU process parameters for these phenomena will reveal the behaviour of the polymer especially for the physical behaviour. For mathematical modelling mechanisms of heat generation can be used the studies made by Jiang et al. (Jiang et al. 2009, 2016) and Wu et al. (Wu et al., 2017). Additionally, mathematical modelling of the ultrasonic energy balance performed by Grabalosa et al. (Grabalosa et al. 2015) will also help to acquire knowledge and mathematically describe PPSU ultrasonic micro-moulding process.

Performed experiments showed that degradation is responsible for reducing the properties of the samples and the probability is more likely in samples exposed for long duration of ultrasonic vibration. Micrographs of specimens with the highest tensile strength show absence of pores contrary to the samples with low tensile strength, whose surface contains a large numbers of holes. This sample structure can be explained by cavitation process which is also dependent on the parameters adopted. Samples fabricated within the same amplitude but different velocities and ultrasonic time allowed to observe that low pressure inside the chamber makes the cavitation effect more intensive (the bubbles are under resistance).

Other important issue raised in this thesis consider the effect of the weld line on the tensile strength of PPSU samples achieved from ultrasonic and conventional technology. Results showed that using appropriate process parameters it is possible to obtain weld line samples with strengths similar to the samples without weld lines. Moreover, performed experiments proved relationship between the V-notch depth and tensile strength. Increasing amplitude value decreases the V-notch depth, which consequently improves the mechanical properties of the samples. This may be explained by the fact that amplitude level has a significant impact on the interfacial friction phenomena and directly affects the melting temperature. Moreover, it is known from the conventional moulding process, that higher temperature decrease the size of the V-notch.

6.2. Ultrasonic micro-moulding of PEEK

Experiments performed with the PEEK polymer using ultrasonic micro-moulding technology allowed to investigate the process behaviour and determine process parameters appropriate to produce parts with high tensile strength.
Polyetheretherketone as a semi-crystalline polymer is characterised by a sharp melting point and requires high level of heat energy to break down the crystalline structure. Results show that an amplitude of 46.4 μm is insufficient to melt the polymeric content even in the case of the maximum available in the machine ultrasonic vibration time of 10 s. Despite the lack of cavity filling, the beginning of the plastification process could be observed close to the sonotrode, where energy is concentrated. Moreover, long vibration time combined with the

low pressure caused the polymer to be degraded by cavitation phenomena. Higher amplitude values of 52.2 and 58 μm respectively led to plasticize whole volume of pellets. The highest amplitude allowed to use higher values of plunger velocity in comparison to lower amplitude. Conclusions are similar to that from processing PPSU material and confirms the importance of amplitude parameter as the most responsible for the energy supplied. Tests with the amplitude of 58 μm permitted produced parts characterised by the best visual quality.

Processing of PEEK polymers using ultrasonic vibration as a source of energy has a very narrow processing window, where only two sets of parameters were capable to produce parts without signs of degradation and crystallinity level close to the pure granulates.

Using amplitude of 58 μm, plunger velocity of 6 mm/s and 6.5 s of vibration time it is possible to manufacture specimens with the average tensile strength of 87.4 MPa, which is comparable to the specimens from conventional micro injection moulding process (87.6 MPa).

6.3. Results and discussion summary

The main results from the Chapters 3, 4 and 5 are below:

1. Amplitude value has the most impact among the others parameters on the processing of PPSU polymers.
2. Each amplitude value is appropriate to achieving high quality PPSU samples but only combined with the appropriate values of others processing parameters.
3. An amplitude of 40.6 μm is the minimum value necessary to melt the entire volume of the PPSU pellet.
4. The maximum available amplitude of 58 μm allowed to obtain the largest number of PPSU samples.
5. Polymer degradation lowered the mechanical properties, but only if this occurred in the fracture region of the PPSU sample.
6. Increasing the duration of ultrasonic exposure time increases the risk of PPSU polymer degradation due to cavitation.
7. Mathematical model proposed to predict the mechanical strength of PPSU samples within the range 61-67 MPa is characterized by relative approximation error of 10%.
8. Weld line strength increased with increasing amplitude level of PPSU samples.
9. Both the ultrasonic and conventional process are able to obtain weld line samples with strengths similar to the samples without weld lines.
10. There is a relationship between the V-notch depth and the tensile strength of PPSU samples. This is based on the principle that the smaller the depth, the higher the strength.
11. Amplitude of 52.2 μm is the minimum value capable of melting the PEEK polymer.
12. Using mould temperature of 180°C allows to obtain real crystallinity level close to the pure granulates from the supplier.
13. Amplitude of 58 μm allows to obtain the best quality PEEK samples.
14. Using appropriate process parameters, it is possible to achieve PEEK samples with the tensile strength comparable to the conventional micro-moulding technology.

Chapter 7. Conclusions and outlook

Chapter 7 presents the conclusions of the Thesis, summarizes the main contributions and introduce possible further works. At the end of the chapter is presented the list of publications.

7.1. Conclusions

The work performed in Chapter 3 and Chapter 4 has led to the following conclusions:

1. PPSU polymers can be processed by ultrasonic micro-moulding technology from different process parameters but considering the interaction between them.

2. Amplitude parameter has the greatest influence on the process success.

3. Cavitation bubbles are mainly responsible for polymer degradation during the ultrasonic process.

4. Probability of PPSU polymer degradation rise with increase of ultrasonic vibration exposure time.

5. Using appropriate process parameters in ultrasonic micro-moulding process, the absence of weld line do not reduce tensile strength of the PPSU samples.

6. Weld line strength in specimens fabricated from ultrasonic micro-moulding technology is comparable to those from the conventional injection micro-moulding technology.

7. Magnification of V-notch depth reduce the strength of the weld line.

8. Higher amplitude parameter lead to increase the weld line strength.

According to Chapter 5 these are the findings:

1. Processing the PEEK polymers using ultrasonic micro-moulding technology is possible.

2. Process parameters such as amplitude, speed and ultrasonic time are closely interlinked and each influenced the other.

3. Higher amplitude parameter allows produce parts with better mechanical properties.

4. The average tensile strength from one set of parameters is comparable to the value from injection moulding process.

The knowledge provided with this study certainly will enrich state of the art of the ultrasonic micro-moulding process. Furthermore, results and observations from processing of the polymers characterised by top of the class properties by ultrasonic micro-moulding technology, definitely can serve as a guidelines on processing condition.

7.2. Main contributions

The main contributions of the work presented in the Thesis are summarized below:

1. Chapter 3 focuses on the correlation between process parameters (amplitude, plunger velocity and ultrasonic time) and their influence on tensile strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process.

2. Mathematical model for selecting the appropriate values for the input process parameters required to produce high strength PPSU parts was developed also in Chapter 3.

3. Analysis of weld line formation in ultrasonic micro-moulding process and its effect on the mechanical property of PPSU polymer are presented in the Chapter 4.

4. Chapter 5 shows the investigation of processing parameters and their influence when processing the PEEK polymer successfully.

7.3. Further work

The suggested future work to continue in research of ultrasonic micro-moulding process are the following:

1. Ultrasonic plastification mechanism of PEEK and PPSU polymers.

Investigations of plastification mechanism of these high performance polymers will allow to understand the heating generation and what parameters affect them. Knowledge of the temperature distribution during plastification permit to control the melting phase and identify the conditions/temperatures when the materials will overheat.

2. Modelling the ultrasonic micro-moulding plastification process.

The process of plastification is the most important stage in the ultrasonic micro-moulding. In this step, the polymeric material can be both degraded and not melted completely. Modelling of the plastification process allow to predict the values of parameters on the melting behaviour, which in turn will reduce the need for many practical tests.

3. Influence of initial shape of material on stability in ultrasonic micro-moulding process.

The invariability of the initial conditions before each one cycle certainly affects the repeatability of the ultrasonic micro-moulding process. Commercially available polymeric granulate are deliver in various shape and size. Moreover, polymers before the start of plastification is placed into the chamber in a random position. All of these factors can cause the risk of a different process conditions, which may influence of the parts properties and process stability.

4. Processing new polymeric materials via ultrasonic micro-moulding process.

Processing new polymeric materials by ultrasonic micro-moulding is the basis for the development of technology. The knowledge of process parameters on the properties of new polymers will extend the portfolio of the applications.

7.4. Thesis results

Lists of the publications presented as chapters of this PhD thesis:

Dorf, T., Perkowska, K., Janiszewska, M., Ferrer, I., and Ciurana, J. (2018). Effect of the main process parameters on the mechanical strength of polyphenylsulfone (PPSU) in ultrasonic micro-moulding process. Ultrasonics Sonochemistry *46*, 46–58.

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