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

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Abstract

One of the advantages to using ultrasonic micro-moulding technology is that even single micro parts can be manufactured, thus providing a potential solution for processing expensive polymers in low-volume customized production.
In this paper, downscaled samples made from combinations of the main process parameters, in this case amplitude, plunger velocity and ultrasonic exposure time, were subjected to tensile strength tests. Then, samples characterised by the highest and lowest tensile strength were analysed by a scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR).

Results show not only the correlation between the process parameters themselves, but also the influence they have on the mechanical properties of polyphenylsulfone (PPSU). Experiments demonstrated a high degree of dependence between process parameters and mechanical properties, thus a mathematical model describing the process was proposed. The model can be a useful 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.

Results also indicate that the ultrasonic vibration time influence on the part degradation. 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.

Key words: ultrasonic micro-moulding; ultrasound technology; polyphenylsulfone; PPSU; amplitude; velocity, degradation.

1. INTRODUCTION

In recent years, an alternative technology for producing micro parts using an ultrasonic vibration (>20kHz) 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. [1] reported on the ability to plasticize polymer materials using ultrasonic energy. Their project described a prototype for a new micro injection-moulding machine that would decrease the minimum shot weight [2]. In the first step of the project, they were able to reduce the sprue to about 15 to 20mg. 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. [3] 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 [4] 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 7s) 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. [5]. 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 7mm/s.

The effects ultrasonic vibration has on the physical and chemical properties of polylactide (PLA) micro-moulding processing was described by Sacristán et al. [6]. 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 48.1µm amplitude with 3bar 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. [7] 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. [8] demostrated 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. [9]. 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.

Althought some studies on ultrasonic micro-moulding technology using the knowledge about thermoplastic materials processed so far ahave 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 GY1137 polyphenylsulfone used in this study is a commercially available material manufactured by Solvay Ltd. It is a fully aromatic polymer which chemical structure given in Figure 1. [10].

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 [11] [12].

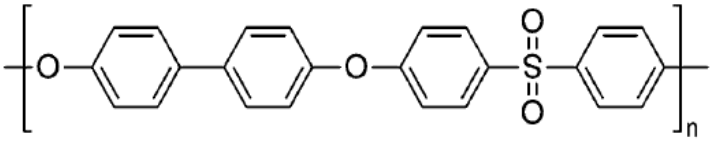


Fig. 1. Chemical structure of PPSU (polyphenylsulfone).

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) [13]. 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). 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 [14]. As the polymer must be dried to avoid cosmetic defects in the resulting part, the external standard dryer of an injection molding machine was used for this purpose.

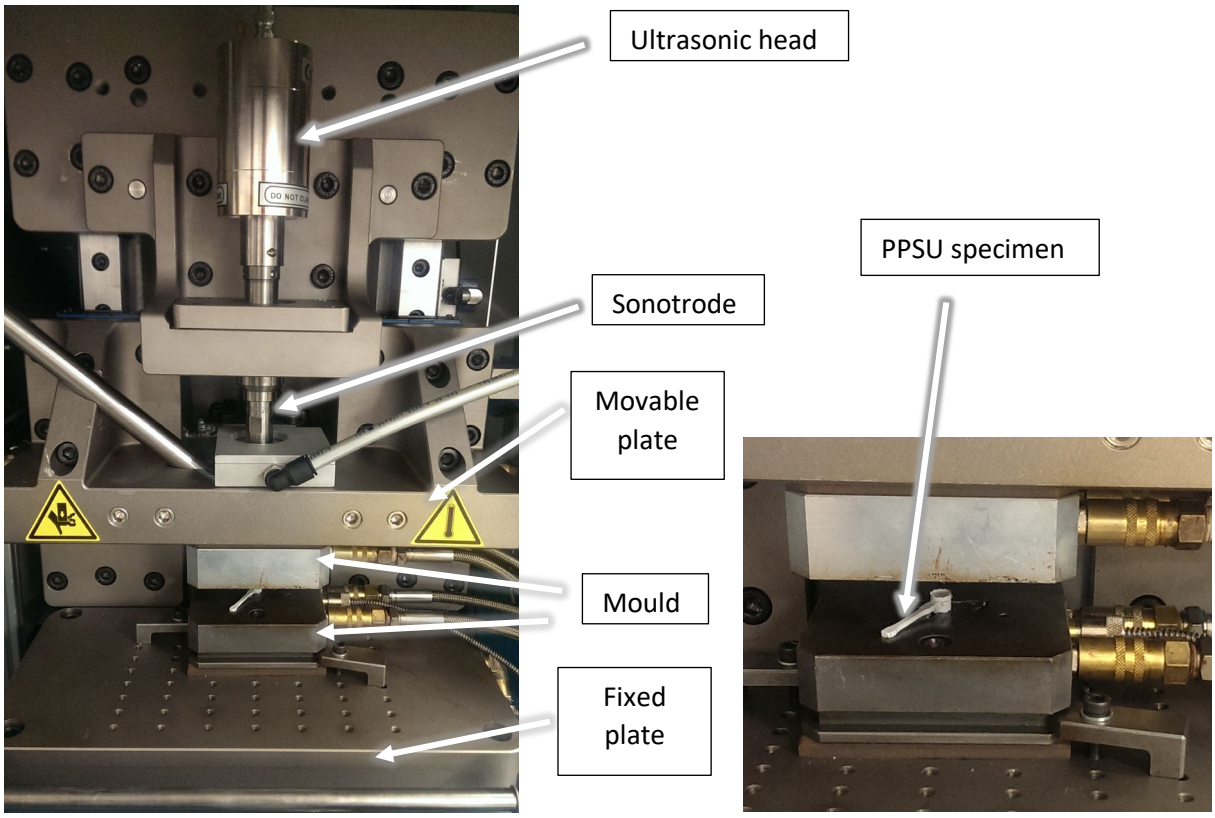


Fig.2. Experimental setup: a) ultrasonic moulding machine, b) mould and specimen

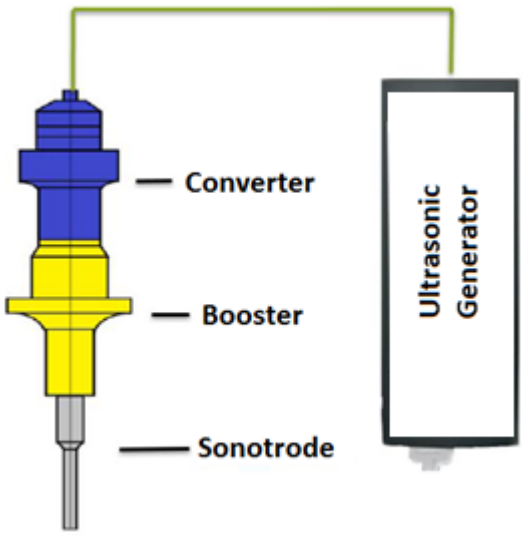


Fig.3. Ultrasonic equipment

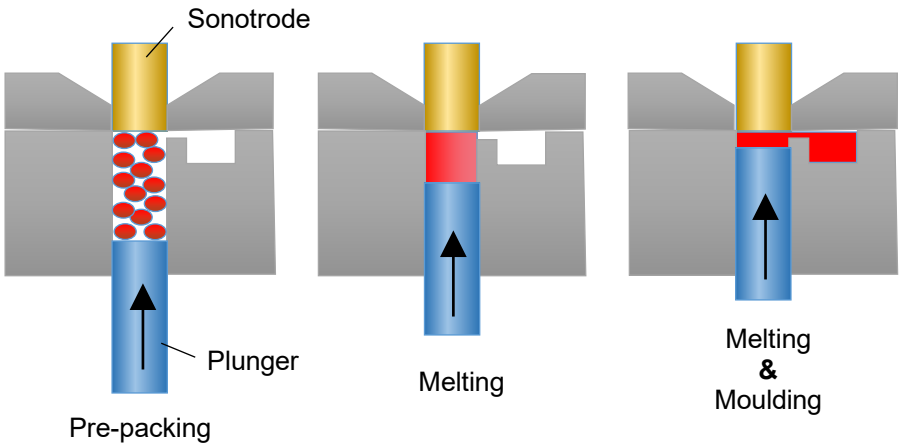


Fig.4. Scheme of the ultrasonic micro-moulding process

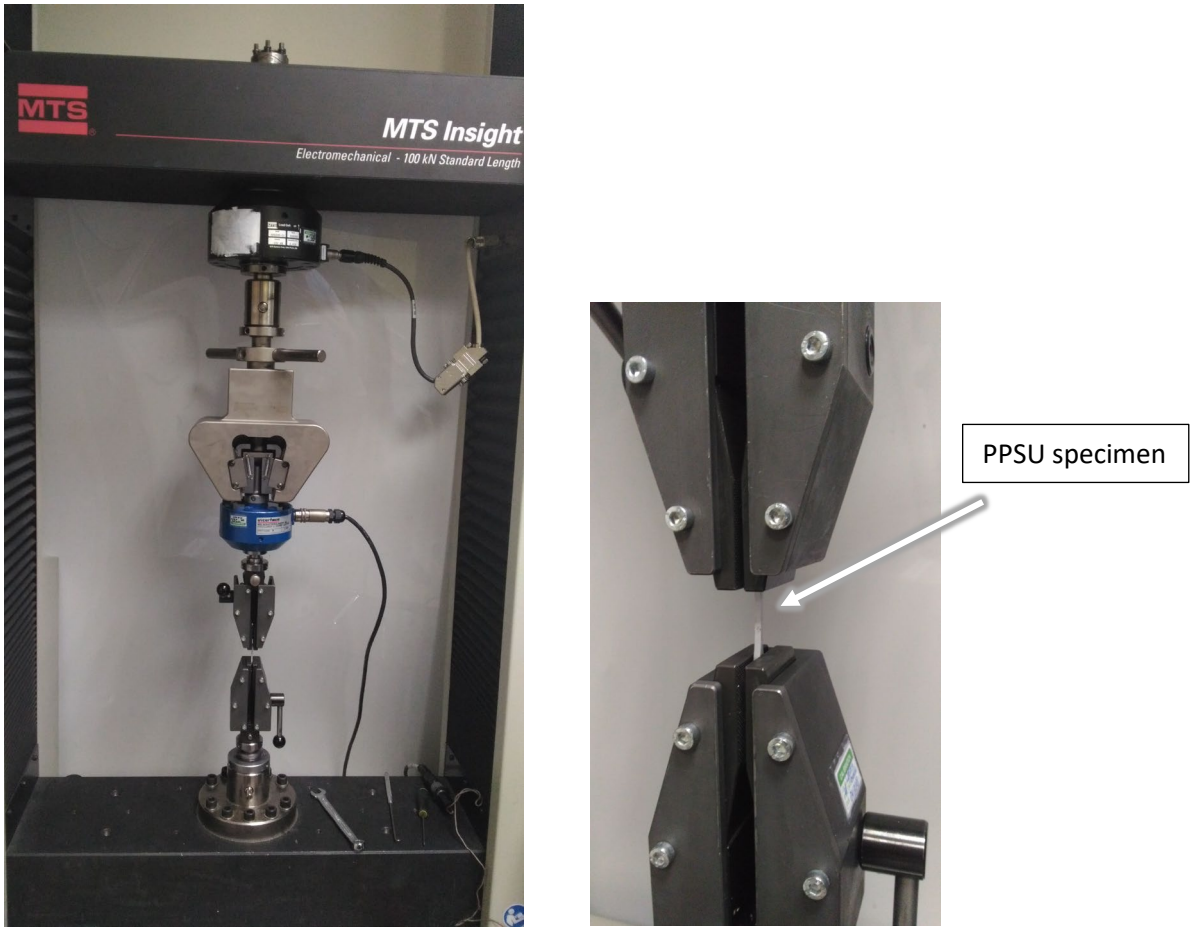


Fig.5. Tensile machine used in the tests.

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 5mm/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 FTIR-ATR.

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

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.

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 method. The combination of two methods makes the algorithm characterized by relatively low computational complexity and allows the approximation of any function of several variables [15],[16].

LMA is used for solution Nonlinear Least Squares Minimization problem which is given the following function:

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

Where is y experimental meansurements. 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 coeffcients of function.

The step of the LM method is given by the formula:

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

where:

$\vec{e}$- vector of approximating error:

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

J- Jacobian matrix:

$$J_{ij} = \frac{\partial e(\vec{x}_i, \vec{\alpha})}{\partial \alpha_j} \quad (4)$$

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 [17], [18]. It is also used for modelling chemical and physical phenomena (e.g. in the creation of models: degradation of polymers [19], strength of materials [20]). 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 Figure 6 and Table 2.

Table 2. Tensile strength value for different amplitude $\sigma_M \pm s$. 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±1	69±1	60±9	52±16	13±23*
	9	-	-	49±1	63±1	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)

* 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

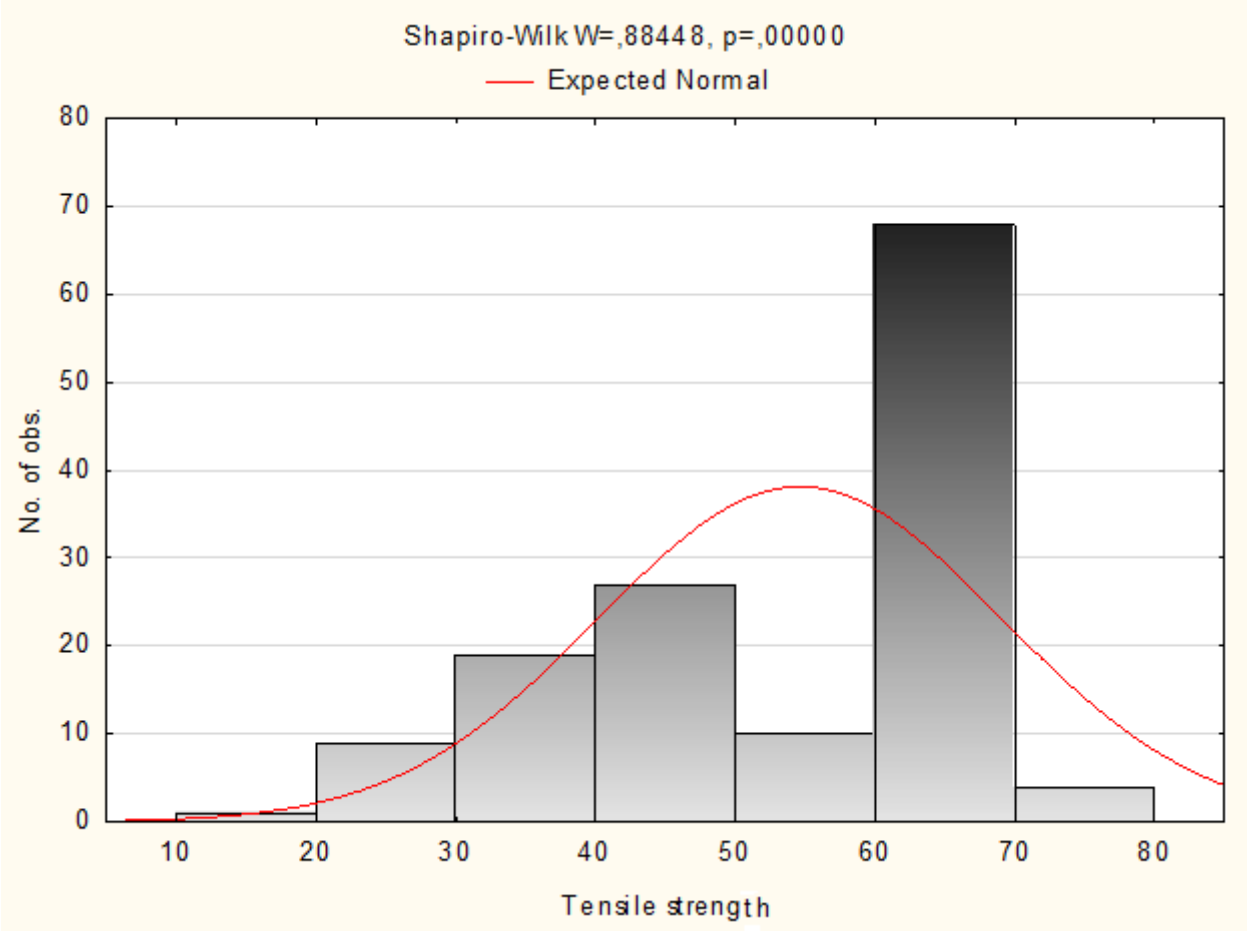
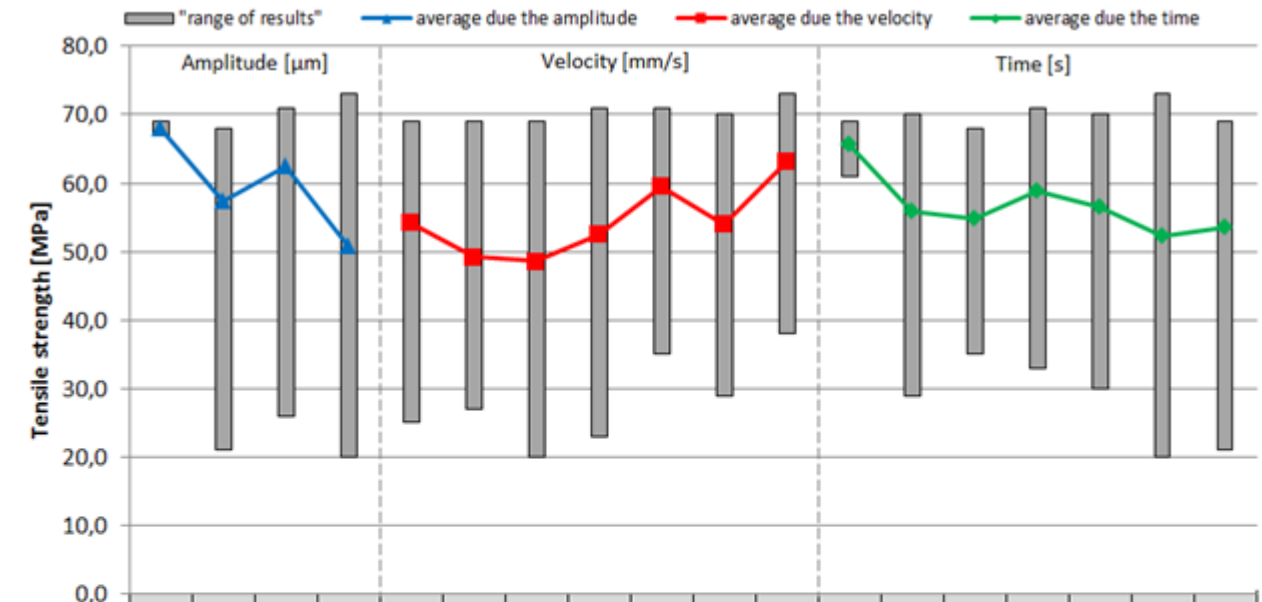


Fig.6. Histogram of tensile strength test results

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%

The distribution of experimental data is not normal. In addition, they are characterized by a large spread. These indicates that the 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.)



	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

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 Figure 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 48MPa, 2nd 44MPa, 3rd 71MPa) 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.

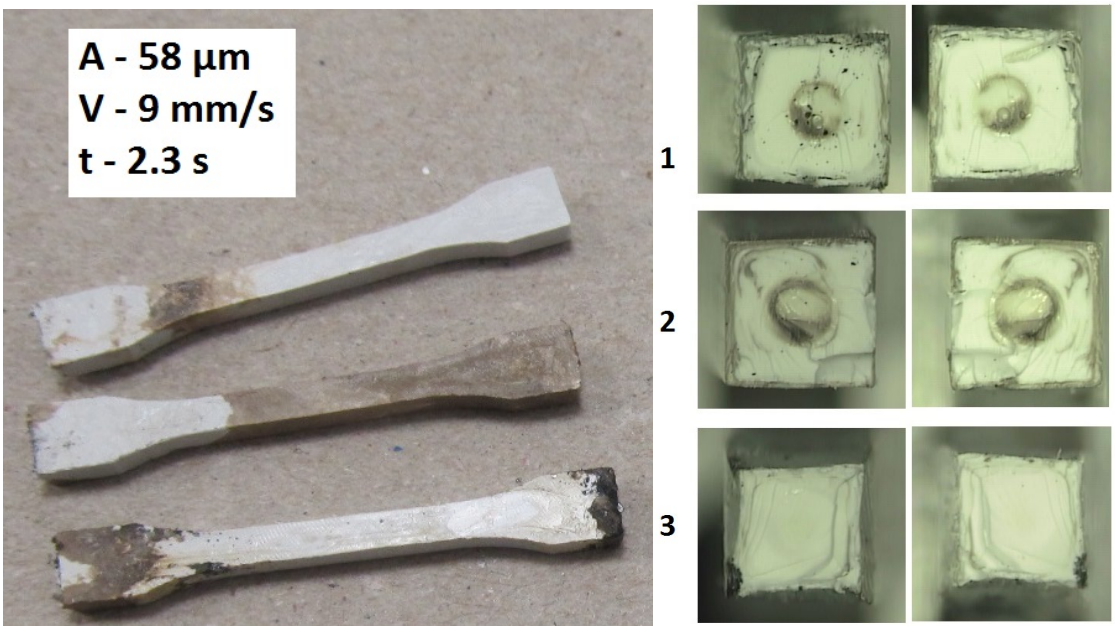


Fig.8. Samples characterised by high standard deviation (σ_M=54±15) and fracture surface at 40X

Figure 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 [4] - 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, causing less resistance to bubble growth. 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 [21].

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.

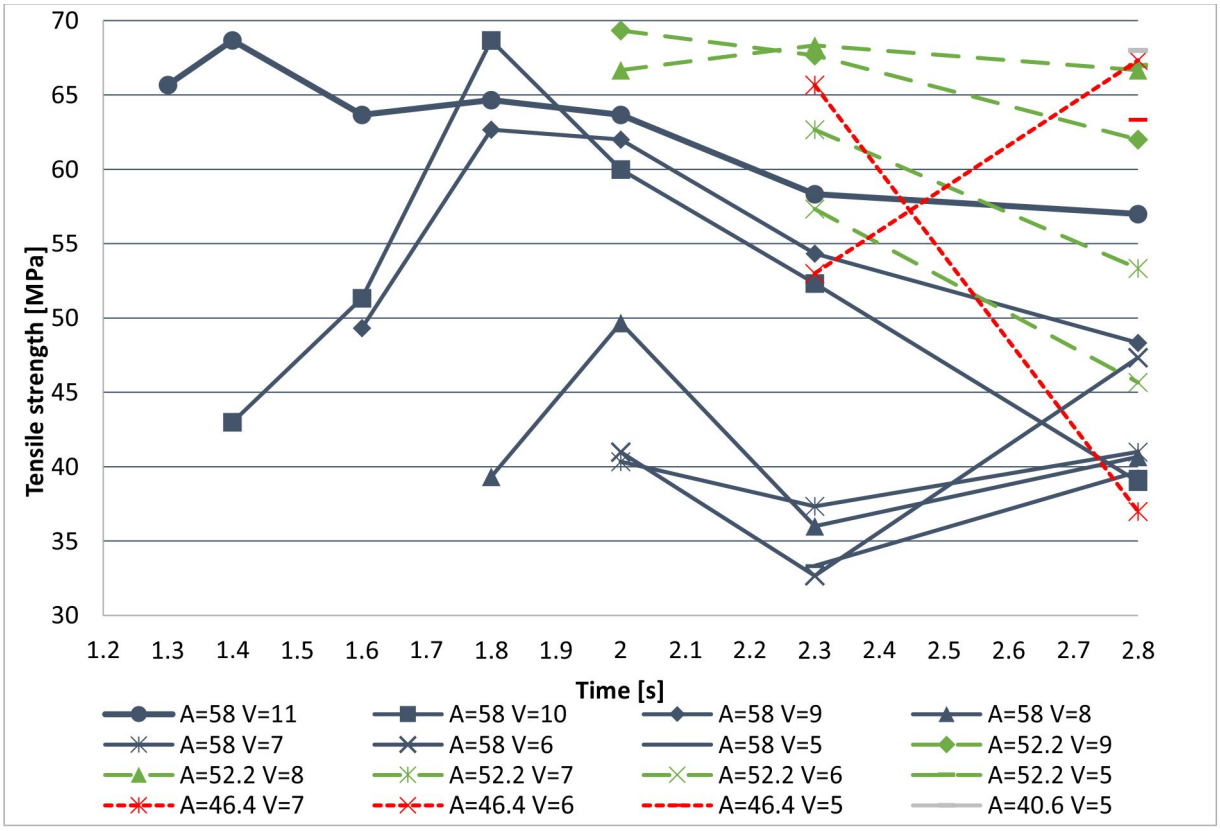
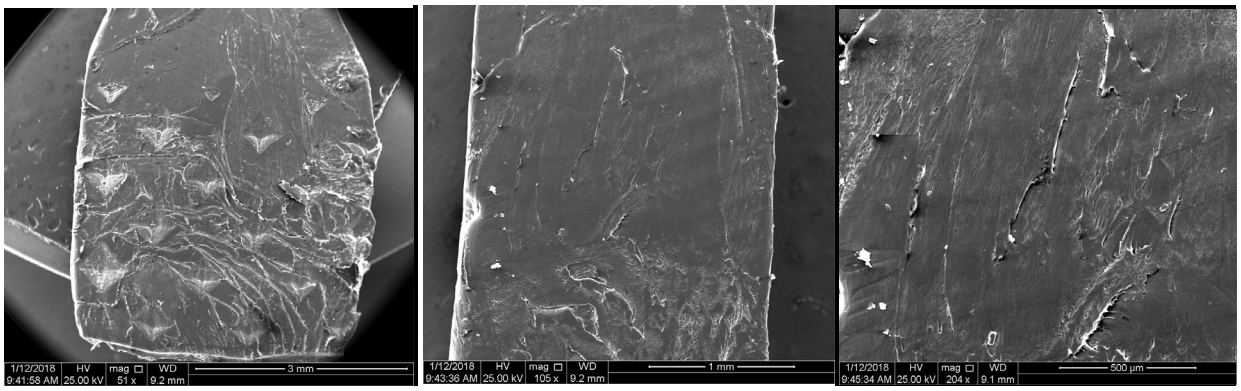


Fig.9. Graph of dependence of input parameters on the tensile strength values

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

a)



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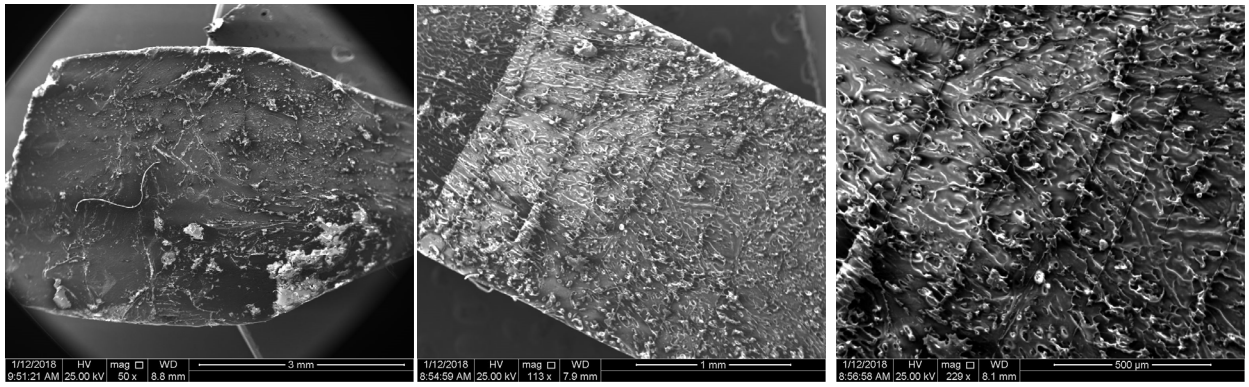


c)

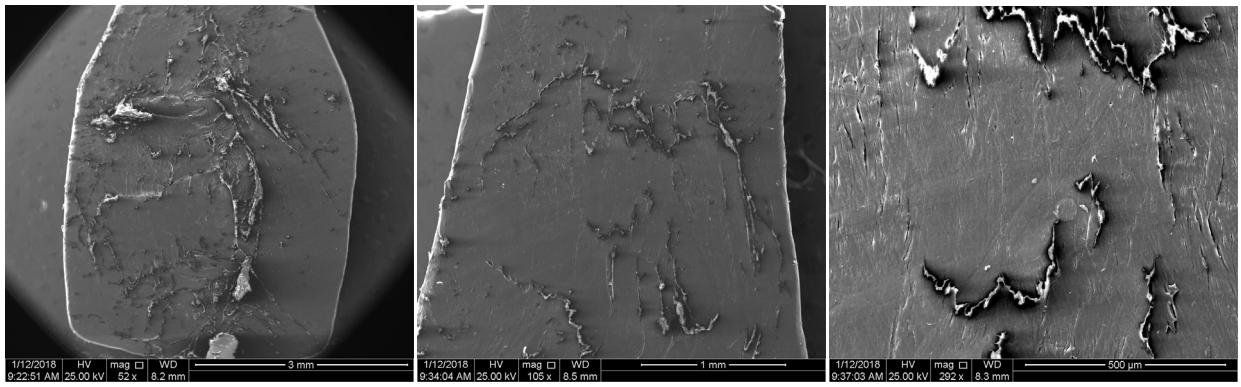


Fig. 10. SEM micrographs of specimens processed with combinations of parameters no. 2 (a), 48 (b) and 196 (c) in resolution 3 mm, 1 mm and 500 µm.

Figure 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.

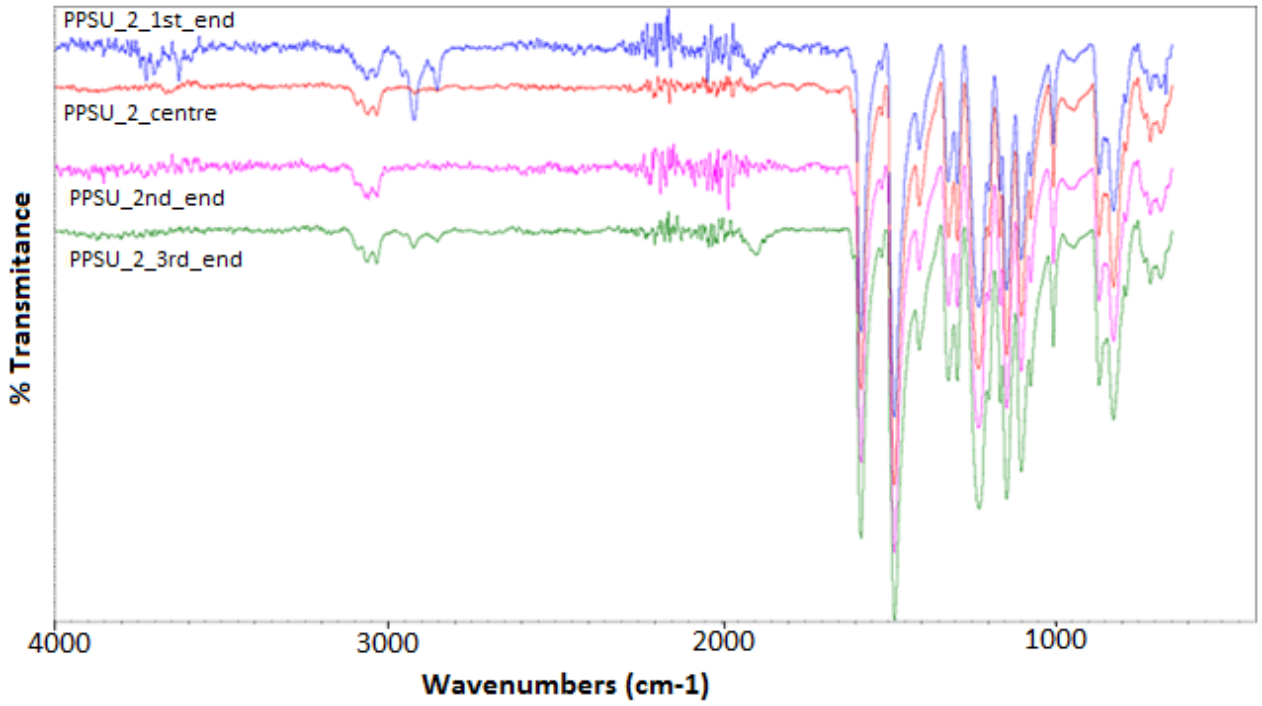
3.3. *Effects of ultrasonic vibration on chemical characteristics of PPSU*

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

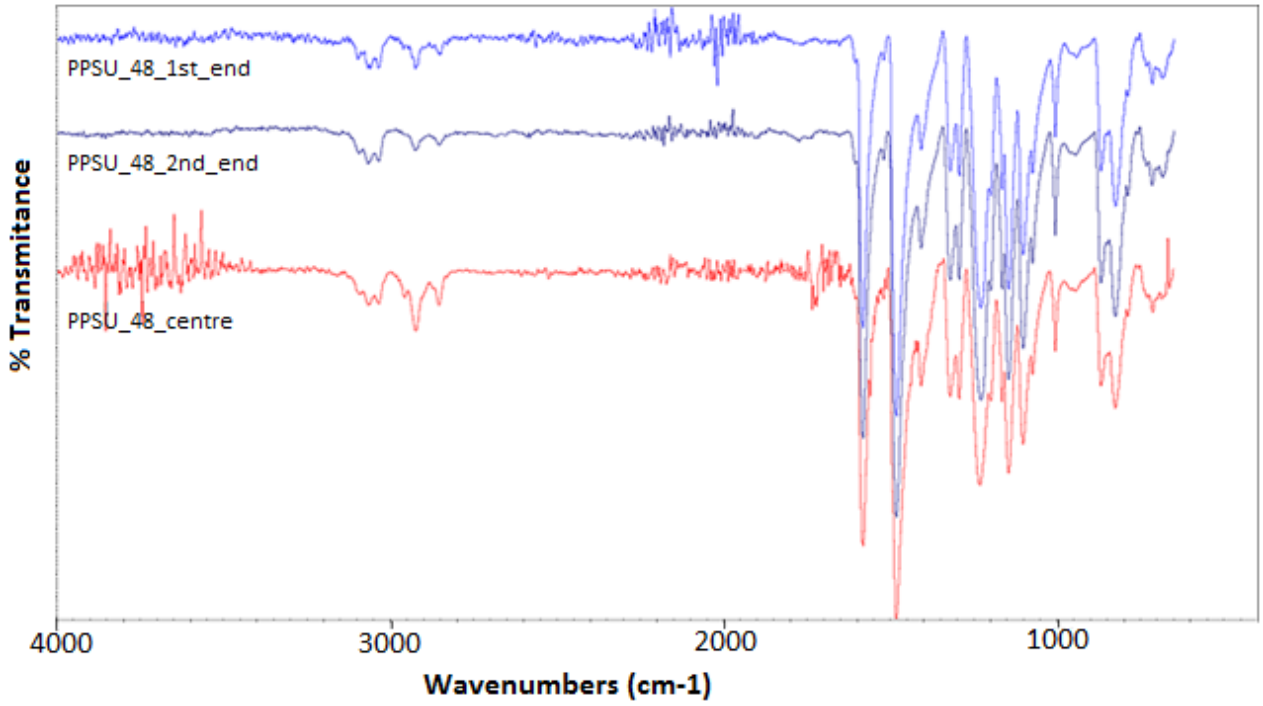
visually visible at highly degraded samples. Three different sections of specimens, processed with the chosen set of parameters, were investigated: the centre and two ends.

In Figure 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 [22],[23].

a)



b)



c)

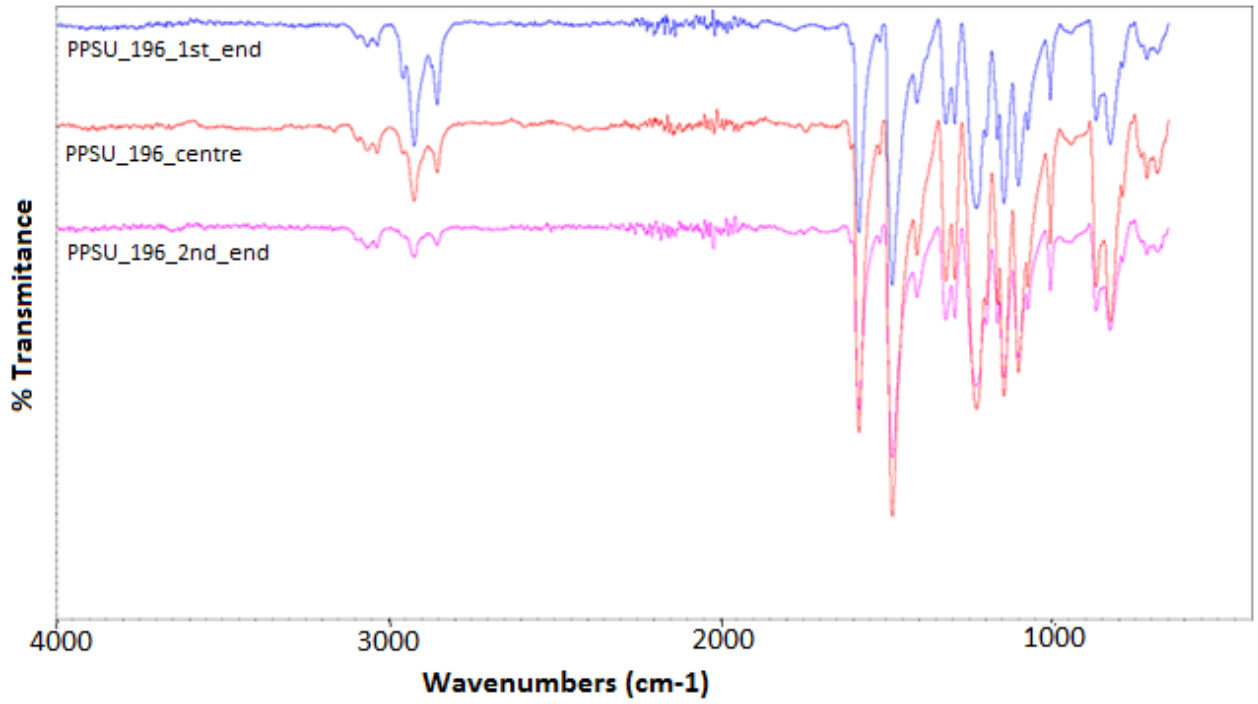


Fig. 11. FTIR ATR spectra of specimens processed with combinations of parameters no.: a) 2, b) 48 and c) 196.

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 Figure 11a there are four

spectrum). 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. [8] 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.

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:

$$y = \alpha_0 + \sum_{i=1}^{n} \alpha_i x_i + \sum_{i=1,j=2}^{n} \alpha_{ij} x_i x_j + \sum_{i=1}^{n} \alpha_{ii} x_i^2 + \alpha_{i,i+1,\dots,n} \prod_{i=1}^{n} x_i \pm \varepsilon \quad (5)$$

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 (1) with the assumption that x_1=A, x_2=V, x_3=t and y=σ_M we obtain:

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

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:

$$
\begin{aligned}
for\ A = 58{,}0 &\begin{cases} V \in (10;11] \rightarrow t \in [1.3;2.8] \\ V \in (9;10] \rightarrow t \in [1.4;2.8] \\ V \in (8;9] \rightarrow t \in [1.6;2.8] \\ V \in (7;8] \rightarrow t \in [1.8;2.8] \\ V \in (6;7] \rightarrow t \in [2.0;2.8] \\ V \in (5;6] \rightarrow t \in [2.0;2.8] \\ V = 5 \rightarrow t \in [2.3;2.8] \end{cases} \\
for\ A = 52{,}2 &\begin{cases} V \in (8;9] \rightarrow t \in [2.0;2.8] \\ V \in (7;8] \rightarrow t \in [2.0;2.8] \\ V \in (6;7] \rightarrow t \in [2.3;2.8] \\ V \in (5;6] \rightarrow t \in [2.3;2.8] \\ V = 5 \rightarrow t = 2.8 \end{cases} \\
for\ A = 46{,}4 &\begin{cases} V \in (6;7] \rightarrow t \in [2.3;2.8] \\ V \in (5;6] \rightarrow t \in [2.3;2.8] \\ V = 5 \rightarrow t = 2.8 \end{cases} \\
for\ A = 40{,}6 &\{ V = 5 \rightarrow t = 2.8
\end{aligned}
$$

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 $\sigma_M \geq 65\ MPa$. 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 (1) and (4), the function of the objective is:

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

and Jacobian matrix:

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

Using the gnuplot 5.0, the model coefficients for the equation (6) were estimated:

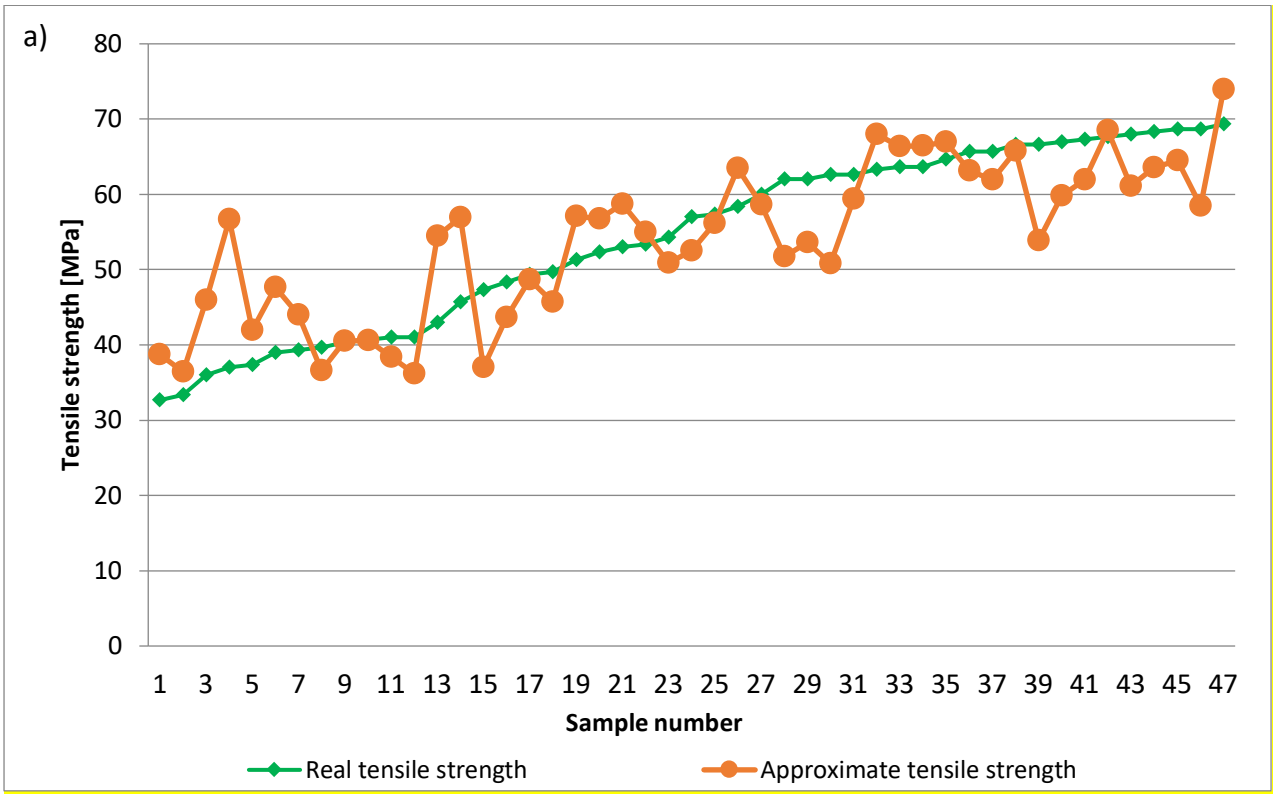
$$
\begin{aligned}
\sigma_M = -1655.3 + 39.8A + 162.0V + 549.8t - 2.7AV - 7.9At - 71.3Vt + \\
-0.2A^2 + 0.4V^2 - 14.8t^2 - 1.17AVt \pm 7.9
\end{aligned}
\tag{9}
$$

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

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 characterized by the greatest correlation with others (α12, α13, α23). The obtained models were characterized 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 (2).



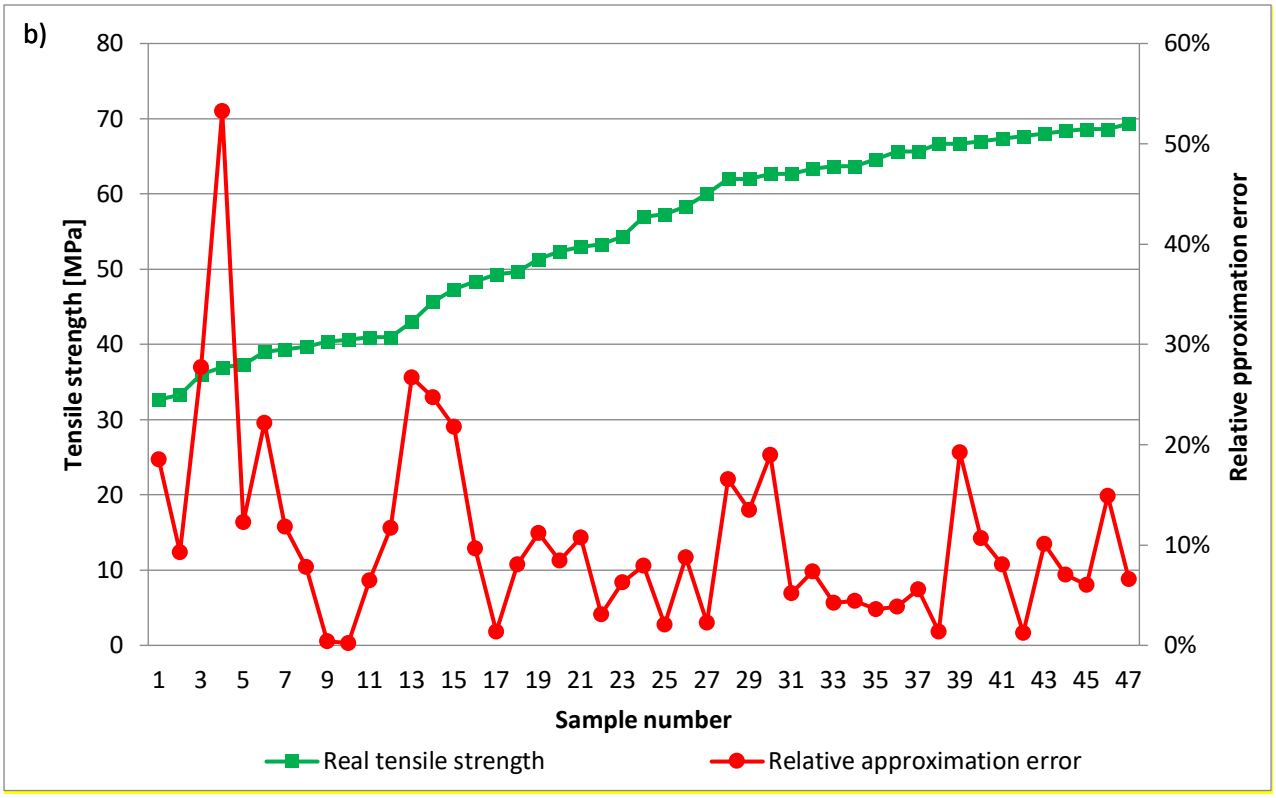


Fig.12. Approximation results: a) real tensile strength and approximate tensile strength and b) real tensile strength and relative approximation error.

According to the charts in Figure 12, 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.

SEM analysis show that 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.

5. ACKNOWLEDGEMENTS

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