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DEVELOPMENT OF ANNEALING PROCESS FOR INJECTION MOLDED PPSU FITTINGS TO REDUCE RESIDUAL STRESSES

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Avainsanat: lämpökäsittely, PPSU, polyfenyylisulfoni, ruiskuvalu, amorfinen, polymeeri, jäännösjännitys, putkiyhde.

Tutkimuksen päätavoitteena on selvittää, miten ruiskuvalettujen PPSU putkiyhteiden jäännösjännitysten minimoimisessa käytettävää hehkutusmenetelmää voidaan nopeuttaa ja tehostaa. Tavoitteena on myös karakterisoida lämpökäsittelystä koituvat mekaaniset, kemialliset ja fysikaaliset vaikutukset PPSU putkiyhteille, määritellä toivotut vaikutukset, sekä testata ja verrata vaihtoehtoisia lämpökäsittelyparametreja. Tutkimustyö on tehty Uponor Suomi Oy:lle Nastolan tehtaalle, jossa PPSU putkiyhteitä valmistetaan LVI-tuotemarkkinoille maailmalaajuisesti. Tutkimus toteutettiin vuosina 2017-2019. Tutkimuksen laajuus on 30 op, mikä vastaa noin puolen vuoden työmäärää. Pääasiallisena tutkimusmenetelmänä on PPSU putkiyhteiden jäännösjännitystason määrittäminen kemiallisesti (MEK-testi). Kemiallisen testauksen tuloksista päätellään hehkutusparametrien vaikutus jäännösjännitystasoon. Hehkutuksen vaikutusta putkiyhteiden fysikaalisiin ominaisuuksiin tutkitaan mittaamalla tuotteiden halkaisija, pituus ja seinämävahvuus, määrittämällä mittausten keskiarvo ja keskihajonta, sekä laskemalla suhteellinen muutos lämpökäsittelemättömän putkiyhteen fysikaalisiin ominaisuuksiin. Eri hehkutusparametrien vaikutusta PPSU putkiyhteiden mekaanisiin ominaisuuksiin tutkitaan taivutuskokeen avulla. Mitatuista maksimi taivutuslujuuden arvoista [MPa] määritetään keskiarvo, keskihajonta, maksimiarvo ja miniarvo verrattavaksi ja analysoitavaksi. Kirjallisuuskatsauksessa etsitään aikaisempaa tutkimustietoa jäännösjännityksiin vaikuttavista ruiskuvaluparametreista ja designista, PPSU:n materiaaliominaisuuksista, sekä muovituotteiden hehkutusmenetelmistä. Tutkimuksen tuloksena odotetaan löytyvän tietoa, jonka perusteella voidaan löytää optimoitu hehkutusmenetelmä PPSU putkiyhteille, sekä uutta tietoa jäännösjännitysten syntymekanismista ja lämpökäsittelyn vaikutuksesta PPSU putkiyhteiden fysikaalisiin, mekaanisiin ja kemiallisiin ominaisuuksiin.

ABSTRACT

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Development of annealing process for injection molded PPSU fittings to reduce residual stresses

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Examiner(s): Dos. Harri Eskelinen
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Keywords: annealing, PPSU, Polyphenylsulfone, injection molding, amorphous polymer, residual stress, fitting.

The main goal of this study is to reconcile how to precipitate and streamline the annealing method utilized in reducing the residual stresses of the injection molded PPSU fittings. Further goals are to characterize the chemical, physical and mechanical changes caused by annealing in the PPSU fittings, to define the preferred effects and testing and comparing compensatory annealing parameters. The research takes place in Uponor Suomi Oy, Nastola facilities, where PPSU fitting are manufactured for worldwide piping markets. The research is carried out during 2017-2019. The extent of the research is 30 sp which corresponds to a work load of approximately six months. The principal research method is determining the level of residual stresses of PPSU fittings utilizing a chemical testing method (MEK-test). Based on the results of the chemical testing, the influence of the annealing parameters to the residual stress level of the PPSU fittings is defined. The average and the standard deviation of the results from dimensional analysis of as-molded and annealed PPSU fitting are calculated and compared in order to determine the possible changes in length, weight and diameter. Bending test is performed to as-molded PPSU fittings and to PPSU fittings annealed in various temperature and time combinations in order to determine the effect of annealing to the mechanical properties. Maximum, minimum and the average values of the maximum bending stress [MPa] are calculated and compared. In literature research existing information of the effects of injection molding parameters and design on the formation of residual stresses, material properties of PPSU and annealing of polymers is sought. The expected result of this study is to find knowledge, based on which an optimal annealing method for injection molded PPSU fittings can be developed, and new knowledge on the formation of residual stresses in injection molding and the effects of annealing on the chemical, physical and mechanical properties of PPSU fittings.

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The completion of this thesis was a long and rocky road. I would like to thank my spouse and children for giving me the time to concentrate on studying instead of cooking and cleaning. A lot has happened since I initially started to plan the thesis. I changed my job, bought a house, got married and build a garage with my husband. I implemented a new coordinate measuring system, which took almost a year and took part of a huge product group renewal project . So there are a lot of reasons why the completion of this thesis has been a two and a half years project instead of six months, that it should have been. Never the less, the study would have not been as fulfilling if it would have been finished sooner, as the subject has become more and more important to myself and the company I am working. The knowledge has increased, but also the amount of open questions, that need to be resolved in the future.

I want to thank Docent Harri Eskelinen for his patience and support through my studies and the making of this thesis at LUT. He has made me believe in myself and he has also made me understand that sometimes I set the bar a bit too high for myself.

I also want to thank all the professors and support personnel at LUT University. As we were the first group to attend JeDI class, all the personnel at LUT University has done a great job to make our studies possible. Special thanks to my class, JeDI 2015! Without the support from each other’s, it might have been impossible to graduate.

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Minna Nuutinen

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LIST OF SYMBOLS AND ABBREVIATIONS

n= Number of the samples tested

S= Standard error of the mean

T_g= Glass transition temperature

CAE = Computer aided analysis

ESCR= Environmental stress crack resistance

MEK= Methyl Ethyl Ketone

PPSU= polyphenylenesulphone

PSU=polysylfone

1 INTRODUCTION

The goal of this research is to reconcile how to precipitate and streamline the annealing method utilized in reducing residual stresses of injection molded PPSU fittings. Further goals are to characterize the chemical, physical and mechanical changes caused by annealing in the PPSU fittings, to define the preferred effects and testing and comparing compensatory annealing methods. The plan is to study what are the effects of the current batch annealing on the products properties and what is the level of residual stresses before and after the annealing, and to find out how can the same effects be achieved with a shorter annealing time. A more efficient process flow and reduction of manual work phases and further understanding of the annealing process are the possible benefits that can be achieved based on the knowledge gained in this research.

The target company of this research is Uponor Corporation, which manufactures certified products, such as plastic and composite piping, plastic and metal fittings and other components for the building and infrastructure industries. The target company is a global corporation and it's originated from Finland, Lahti area. The company celebrated its 100th birthday in 2018. This research focuses on a heat treatment process taking place in the Plastic Fittings department. The heat treatment process is called annealing and its purpose is to release residual stresses from the injection molded fittings. The residual stresses predispose injection molded amorphous plastic components to chemical frailty. At the moment the annealing process is executed utilizing a traditional batch method, in an industrial convection oven. The plastic fittings are manufactured out of polyphenylenesulphone, PPSU, which is a high performance thermoplastic. The quality of each annealed batch is assured with a testing method, in which the part is predisposed to Methyle Ethyl Ketone (MEK) for two minutes. If the level of residual stresses is less than 4 MPa, the part does not show cracking nor crazing. In case of cracking, the annealing did not effect on the residual stresses as it should have. The current annealing method has been developed in order to eliminate snags and quality deviations and it is on its current state utilitarian but slow. The flow of the production is under development and as the annealing is a separate operation, it needs to be developed to be more efficient and automated. One considered option is to replace the batch method with an in-line annealing, which would be more efficient and a natural sub process in an automated production cell in series production.

1.1 Research background

The meaning of this research is to find knowledge to develop an optional method for the current annealing method to be integrated into the production line. The reductive effect on the residual stresses is not to be lowered due to this change, but the new annealing method is expected to be at least just as effective as the current one in a shorter period of time. In this research the possibility of shorter annealing time without compromising the product quality is studied.

The plastic fittings have been manufactured at the target company since 1997, at first out of polysulfone (PSU) and since 2001 out of PPSU. The annealing has been part of the process since the beginning, as it was realized that the residual stresses could be reduced by utilizing this simple heat treatment method. During the last few years the departments floor space has been reduced due to centralized operations. This has caused pressure to improve the flow in the production process. The future plan is to increase automation in the production and the possibility of automating the annealing process is taken into consideration.

From the point of view of the target company, the aim of this study is to fulfill the quality demands set by the customers and authorities, to increase the level of automation and streamline the annealing process. In the customer point of view the future benefits of this research are that they receive high quality products with reasonable price range due to effective and streamlined production.

In more general level there are some previous researches of annealing, but when it comes to PPSU, not much specific literature or researches are available due to materials high price range and limited amount of PPSU product manufacturers and material suppliers. Equipment manufacturers offer information based on their own devices, but those commercial sources cannot be considered reliable in a scientific point of view. For this reason, this research and its results could be profitable for other plastic product manufacturers.

1.2 Preliminary studies and prior researches

Some testing and short, informal studies has been made of the annealing process previously at Plastic Fittings -department, but no scientific, complete studies have been published. The current information of the reliability and functionality of the current annealing method is based on process planning and development and by utilization of the MEK-test (Methyl Ethyl Ketone) in quality assurance. The residual stresses have been tested from every annealed batch for as long as the annealing has been performed since 1997. Over 3000 MEK-test were done in 2018. Annual testing amounts vary from 1800 to 3100 tests. (Uponor Suomi Oy, 2019.)

According to preliminary literature findings, the residual stresses in the injection molding process is a well-studied subject. Over 700 researches related to residual stresses and injection molding can be found via Scopus. Most of these studies are published in China, where injection molding is widely utilized manufacturing method of plastic parts (Yang, Chen, Lu, & Gao, 2016). 105 researches published in 2009-2018 were related to thermoplastics. Any researches related to residual stresses of PPSU or other sulfone plastics could not be found during literature review. In the literature findings the residual stresses were examined in multiple different methods, but only ten researches related to annealing of thermoplastics was found (Cho;Park Seo;Kim;& Lyu, 2012) (Fan;Yu;Zuo;& Speight, 2017) (Guevara-Morales & Figueroa-López, 2014) (Kamal;Lai-Fook;& Hernandez- Aquilar, 2002) (Katmer, Esen, & Karatas, 2014) (Koslowski & Bonten, 2017) (Siegmann;Kenig;& Buchman, 1987).

1.3 The research problem

In the company under investigation, it has been discovered as practical problems in the current annealing process, that it requires long processing time as the heat distribution is uneven in the treated batch due to poor thermal conductivity of polyphenylsulfone and the large mass of the annealed fittings in the same treatment batch. The method also requires unnecessary operations. The problem in the material technological point of view is formed in defining and reconciling of the material properties, annealing parameters, polymer properties, manufacturing process parameters, fitting geometry and annealing circumstances. In order to solve the practical problem, the presented material technological problem is to be solved also. The department manufactures over 10 000 000 fittings annually, from which approximately 50% are annealed.

This means over 5 000 000 annealed parts annually. Examples of uninstalled S-press fittings (coupler, elbow and tee) utilized in multilayer composite pipe applications are presented in the figure 1. In the figure 2 an example of an installed Quick&Easy T20-20-20 fitting is presented. Quick&Easy fitting are utilized in PEX-pipe applications. Both PPSU fitting groups are produced in outlet size range from 16mm to 63mm. The outlet size indicates the inner diameter of the suitable pipe. (Uponor Suomi Oy, 2019.)

Figure 1. S-Press Coupler, Elbow and Tee fittings, outlet size 20mm (Uponor Corporation, 2019).

Figure 2. Quick&Easy Tee fitting, outlet size 20mm (Uponor Corporation, 2019).

1.4 The goals of the research and the research questions

The main goal of this study is to reconcile how to precipitate and streamline the annealing method utilized in reducing the residual stresses of the injection molded PPSU fittings. Further goals are to characterize the chemical, mechanical and physical changes caused by annealing in the PPSU fittings, to define the preferred effects and testing and comparing compensatory annealing parameters.

In this research the following questions are to be answered :

- How does the residual stress level of the products change in the annealing process and why?
- What options are available for replacing the current annealing method?
    - Is a continuous type of annealing process as efficient in releasing internal stresses as the current batch annealing method as the annealing time needs to be significantly shorter?
- What parameters/ annealing time is sufficient for gaining adequate relaxation of residual stresses and with what methods this should be assured?
    - Is it possible to precipitate the annealing process by rising the processing temperature and what effects does the temperature have on the properties of the products?
- What effects has the annealing parameters have on the chemical, physical and mechanical properties of the PPSU fittings?

1.5 Hypothesis

According to the preliminary researches, at least the following hypothesis can be presented:

1. The residual stress level of the PPSU fittings can be decreased in shorter annealing time, if the annealing temperature is increased from the currently utilized level.
2. Increasing the annealing temperature near to glass transition temperature (T_g) can cause unwanted dimensional changes to the PPSU fittings.
3. The changes in mechanical properties of the PPSU fittings can be controlled more precisely in inline annealing compared to the batch annealing.

4. Batch annealing is more forgiving to the changes in the residual stress level of the as molded PPSU fittings compared to the inline annealing.

1.6 The scope of the research

This research is defined to apply only for the annealing process of injection molded PPSU fittings. The actual investment and practical implementation of the continuous annealing process are not included in this research. Only residual stresses of injection molded PPSU fitting with specified profile are further studied in this research. The result or the testing methods may not be suitable for other thermoplastics or manufacturing methods of plastics. As the amount of variables in injection molding of thermoplastics is endless, only small part of them can be taken into account in this research. This definition is based on preliminary information on the subject, which has been acquired from literature or is based on practical experience.

1.7 Description of the research project

The research is carried out during the year 2017-2019. The research is part of the target company's research and development functions. Both qualitative and quantitative research methods are utilized. The research is initiated with a literature research, in which existing information of the effects of injection molding parameters and design on the formation of residual stresses, material properties of PPSU and annealing of polymers is sought. The principal research method is determining the level of residual stresses of as molded and annealed PPSU fittings utilizing a chemical testing method (MEK-test). Based on the results of the chemical testing, the influence of the annealing parameters to the residual stress level of the PPSU fittings is defined. The average and the standard deviation of the results from dimensional analysis of as-molded and annealed PPSU fitting are calculated and compared in order to determine the possible changes in length, weight and diameter. Bending test is performed to as-molded PPSU fittings and to PPSU fittings annealed in various temperature and time combinations in order to determine the effect of annealing to the mechanical properties. Standard deviation, maximum, minimum and the average values of the bending test results are calculated and compared.

The test pieces (PPSU fittings) are manufactured in the plastic fittings –production utilizing the injection molding machines available on the premises. An infrared oven is utilized as an inline annealing demonstration device.

1.8 Expected results

As results for this research it is expected to find out knowledge about the behavior of the PPSU fittings, when annealed with different methods. On bases of this information, a plan to develop or replace the currently utilized annealing method can be made. It is also expected to receive knowledge of the necessity of annealing of the PPSU fittings.

2 RESIDUAL STRESSES IN INJECTION MOLDED PARTS

In order to understand how the residual stress level can be reduced, the formation of residual stresses in injection molding process should be understood. In this chapter the principals of injection molding machinery, process and processing parameters are explained briefly, concentrating on the factors that affect to the formation of the residual stresses. The basics of the formation mechanism of residual stresses in injection molded parts is explained.

2.1 Injection molding

Injection molding is the most widely utilized manufacturing method of shaped plastic parts, such as toys, technical components and everyday items, as complex parts can be manufactured in a single process step at low costs. Injection molding was invented in the late 1800's by John Wesley Hyatt, who also developed the process able form of celluloid. In the 1940's, as the manufacturing of plastic products became a mass production industry, the screw injection machine was developed by James Henry. Of course the development of the automation technology can be seen in the current models of injection molding machines, but the principals of injection molding process still remains the same. (Bryce, 1996.) (Koslowski & Bonten, 2017.) The basic structure of injection molding machine is presented in the figure 3.

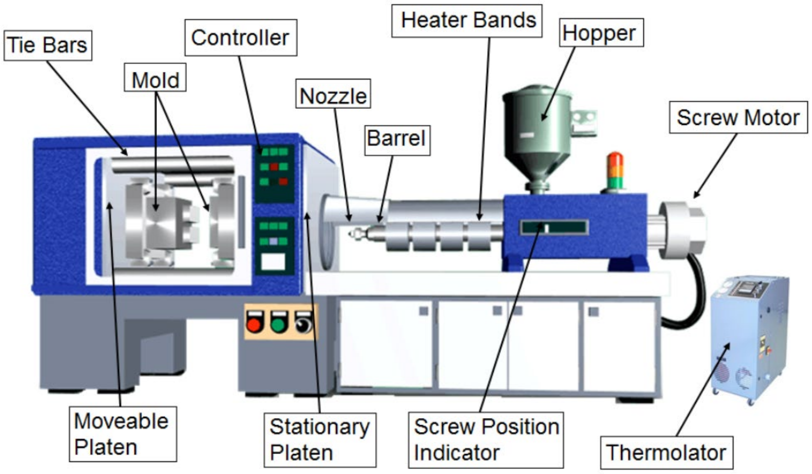


Figure 3. Basic structure of injection molding machine (Beaumont, 2019).

In injection molding process the plastic resin is transported to the hopper, from where it flows to the heating cylinder. Inside the heating cylinder there is a screw, which both rotates and moves back and forward like a piston. The screw rotates and moves backwards in order to collect a dose of molten plastic in front of the it. Then the screw rabidly moves forward and presses the plastic melt in to the closed mold and the packing pressure continues to fill the mold as the material cools down. After the plastic has cooled down and the cavity gate has solidified, the mold opens and the part is removed from the mold either with mechanical ejection pins or with the help of a robot. The main stages of injection molding process are filling, packing, cooling and ejection. Injection molding cycle and the relative time for each part of the cycle is presented in the figure 4. (Guevara-Morales & Figueroa-López, 2014.) (Karthikeyan;Jayabal;Kalyanasundaram;& Boopathi, 2015.)

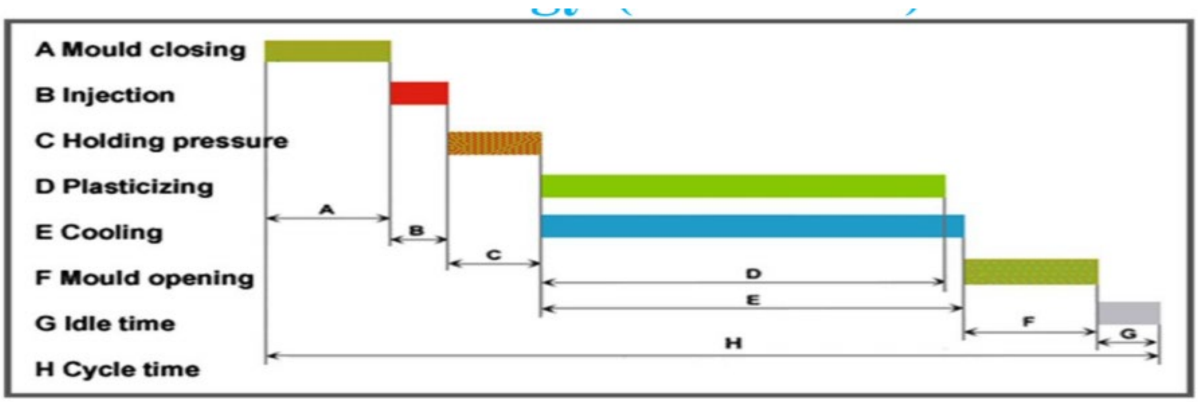


Figure 4. Injection molding cycle (Karthikeyan;Jayabal;Kalyanasundaram;& Boopathi, 2015) .

2.2 Injection molding parameters

According to Bryce (1996), more than 200 different variables have an effect on injection molding process. When one parameter changes, it also affects to other parameters. These 200 parameters include all the variables of the machine and its surroundings, such as ambient temparature, air humidity and dust, so not all of them can be easily conrolled by the operator. For this reason injection molding can be quite challenging process, but not impossible to control, when concentrating to the parameters that can be controlled and affect the most to quality and cost-effectiveness of the production. The processing parameters in injection molding simplified into four main categories by Bryce (1996) are presented in the figure 5. The size of the circle presents the significance of the parameter category. (Bryce, 1996, ss. 29-30)

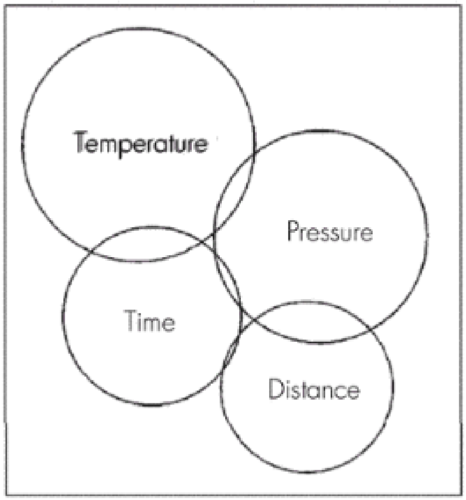


Figure 5. Categories of injection molding parameters scaled on the bases of their effect (Bryce, 1996)

The injection molding parameters in the temperature -group are cylinder temperatures in different heating zones and the mold temperature(s). Also raw material drying temperature can be considered as injection molding parameter in cases, where the raw material needs to be dried. In addition to these parameters, there are numerous temperatures that have an effect on the end quality of the molded product, such as the ambient temperature, the raw material temperature, et cetera, but these parameters are not adjustable by the machine operator. Melt temperature is one of the most significant injection molding parameters, even though it cannot be directly adjusted by the operator. Naturally the temperature in the heating zones have a significant effect on the melt temperature, but also other parameters affect the melt temperature, such as the friction between the raw-material and the screw/cylinder. The melt temperature is not necessarily measured, but in order to control the injection molding process more specifically, it is recommended to measure the melt temperature. The main injection molding parameters related to temperature are presented in the figure 6 (PolyOne, 2019). (Bryce, 1996.) (Yang, Chen, Lu, & Gao, 2016.)

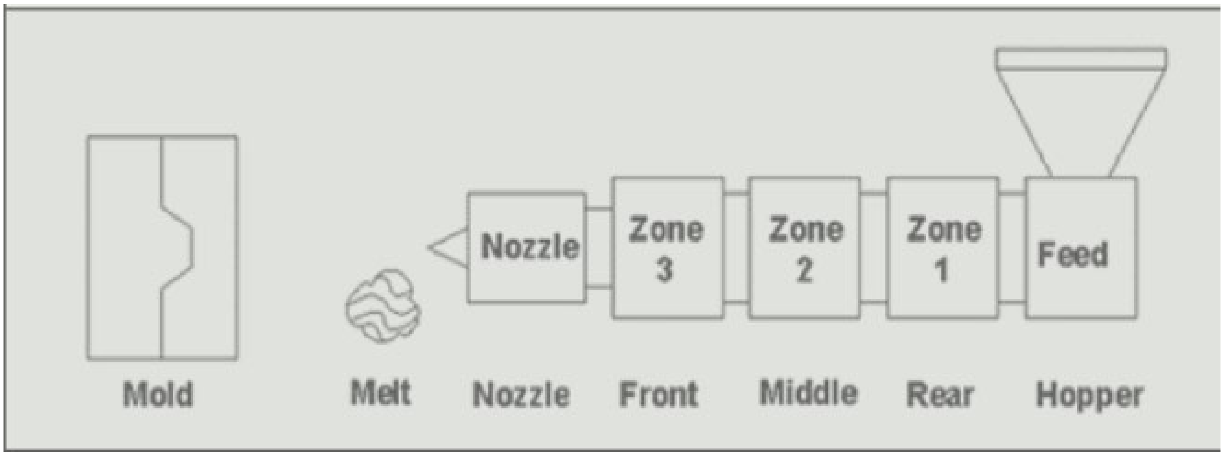


Figure 6. Main temperature related, adjustable and measured parameters in injection molding machine (PolyOne, 2019).

In the Pressure -group of injection molding parameters there are also parameters that can be adjusted by the operator, but parameters that are important to measure. Commonly injection pressure and post injection pressure (or holding pressure) are considered to be the most important of the pressure related parameters in injection molding process. The actual injection pressure is a measured parameter, and the operator can only set a maximum limit to the injection pressure. The user set parameter that affects the most to the level of injection pressure is the injection speed. The actual level of injection pressure is based on the level of the injection speed setting, the viscosity of the plastic melt, and the area of the flow channels. The holding pressure profile is on the other hand a parameter that can be set by the operator. The other injection molding parameters are in example change pressure and backpressure. (Bryce, 1996.) (Yang, Chen, Lu, & Gao, 2016.) Typical pressure profile in injection molding cycle is presented in the figure 7.

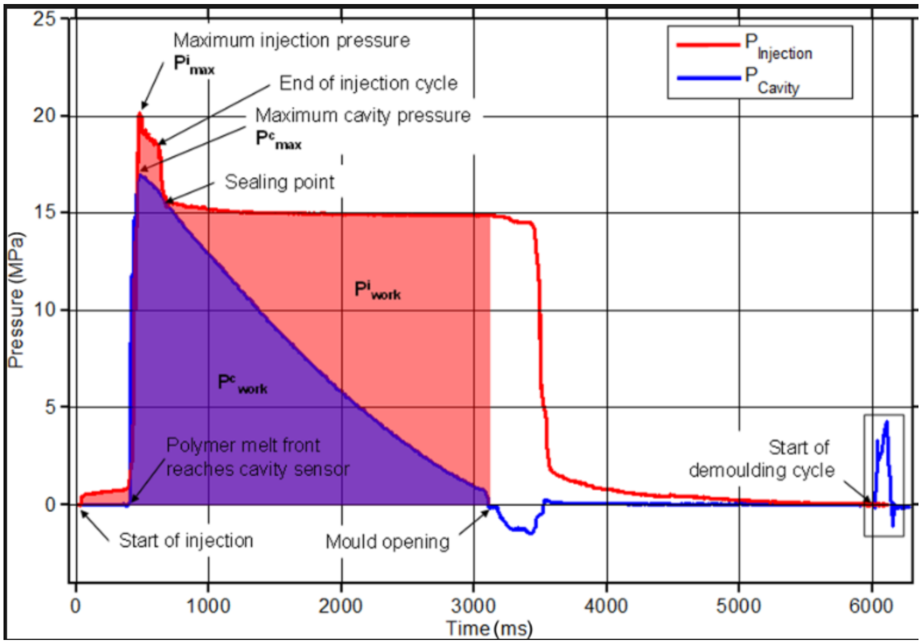


Figure 7. An example of pressure profile during an injection molding cycle (Griffiths;Dimov;Scholz;Tosello;& Rees, 2014.)

Time -gategory includes molding parameters such as plastication time, screw delay time, injection time, change time, holding pressure time, cooling time and cycle time (Bryce, 1996). The relationship between the duration of each main phases of injection molding cycle is presented in the figure 4 (Karthikeyan;Jayabal;Kalyanasundaram;& Boopathi, 2015).

The injection molding parameters related to distance are basically physical moves during the cycle. Shot size is adjusted as the distance, which the screw moves during the filling phase. The screw positions at different stages of the injection molding cycle is presented in the figure 8. The mold opening distance needs to be adjusted based on the size of the part itself and the space for ejection, wheter the part is just dropped down from the mold, or removed by a robot. The ejection travel distance is adjusted so, that the mold fuctions correctly, the ejector pins are positioned correctly (in rear position) when the mold is closed, and the part is efficiently ejected when the mold opens. (Bryce, 1996.)

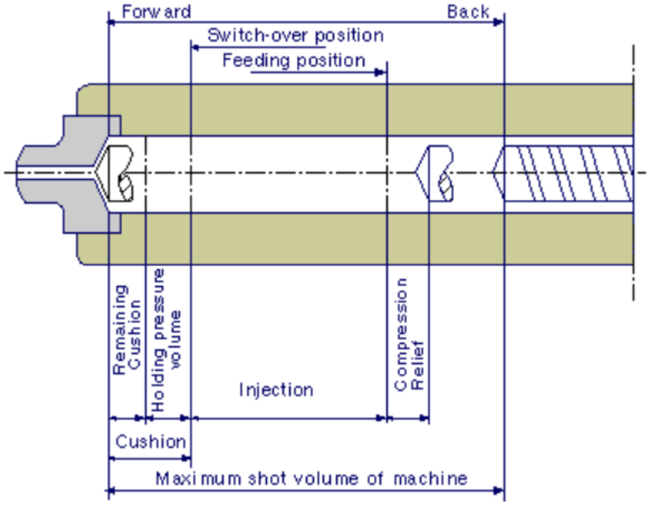
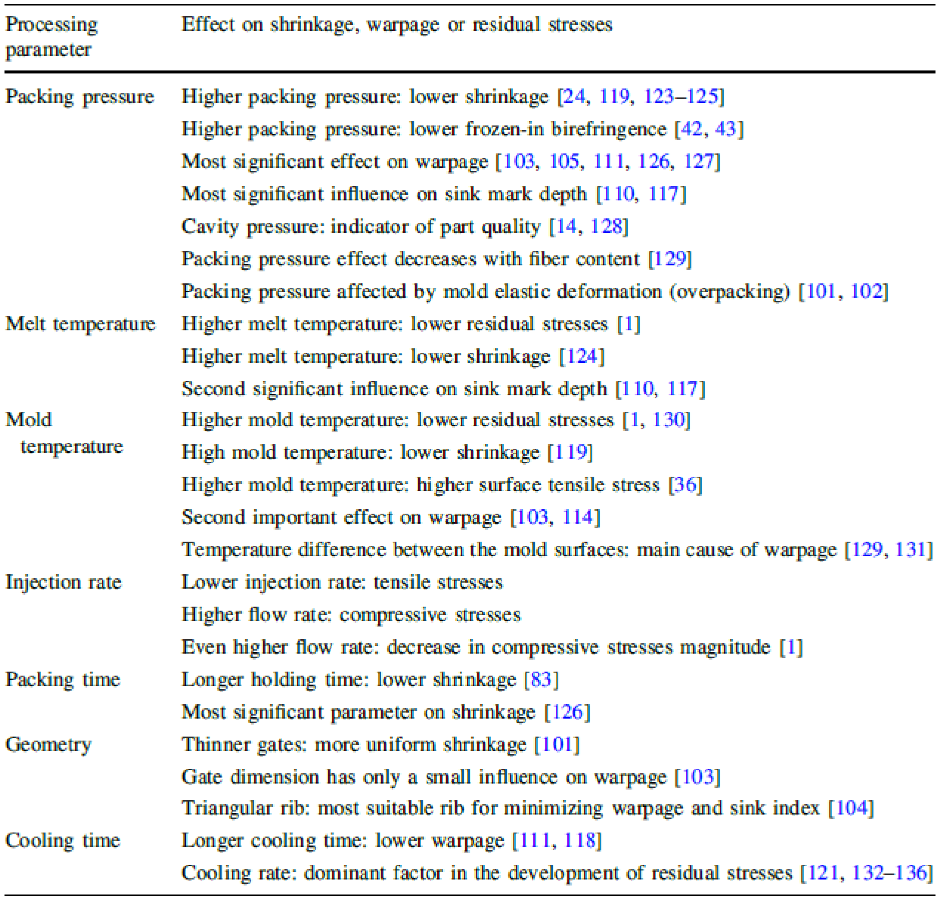


Figure 8. Screw position at different stages of injection molding cycle (Santa Clara University , 2019).

2.3 The effect of injection molding parameters to residual stress formation

In simplified, the residual stresses develop during the mold filling phase due to varying pressure history as the material cools down in the mold. Thermal contraction combined with frozen layer growth causes the long polymer chains to stay in a stress mode. According to Guevara-Morales & Figueroa-López (2014), the factors that have the most effect on the level of residual stresses are packing pressure, mold and melt temperature and the design of the cooling system. The processing parameters and their effect on the residual stresses are presented in the table 1. Also Siegmann;Kenig;& Buchman (1987) state that increased melt and mold temperatures help to reduce compressive surface residual stresses in amorphous polymers. The reductive effect on the residual stresses due to the increased melt temperature is based on “self –annealing” of the core material. (Siegmann;Kenig;& Buchman, 1987). According to Solvay Specialty Polymers (2019) injection parameters and mold and melt temperatures are the main factors also in reducing residual stresses of injection molded PPSU. (Solvay Specialty Polymers, 2019.) (Fan;Yu;Zuo;& Speight, 2017.)

Table 1. Processing parameters and their effect on residual stresses (Guevara-Morales & Figueroa-López, 2014).



Processing parameter	Effect on shrinkage, warpage or residual stresses
Packing pressure	Higher packing pressure: lower shrinkage [24, 119, 123–125]
	Higher packing pressure: lower frozen-in birefringence [42, 43]
	Most significant effect on warpage [103, 105, 111, 126, 127]
	Most significant influence on sink mark depth [110, 117]
	Cavity pressure: indicator of part quality [14, 128]
	Packing pressure effect decreases with fiber content [129]
	Packing pressure affected by mold elastic deformation (overpacking) [101, 102]
Melt temperature	Higher melt temperature: lower residual stresses [1]
	Higher melt temperature: lower shrinkage [124]
	Second significant influence on sink mark depth [110, 117]
Mold temperature	Higher mold temperature: lower residual stresses [1, 130]
	High mold temperature: lower shrinkage [119]
	Higher mold temperature: higher surface tensile stress [36]
	Second important effect on warpage [103, 114]
	Temperature difference between the mold surfaces: main cause of warpage [129, 131]
Injection rate	Lower injection rate: tensile stresses
	Higher flow rate: compressive stresses
	Even higher flow rate: decrease in compressive stresses magnitude [1]
Packing time	Longer holding time: lower shrinkage [83]
	Most significant parameter on shrinkage [126]
Geometry	Thinner gates: more uniform shrinkage [101]
	Gate dimension has only a small influence on warpage [103]
	Triangular rib: most suitable rib for minimizing warpage and sink index [104]
Cooling time	Longer cooling time: lower warpage [111, 118]
	Cooling rate: dominant factor in the development of residual stresses [121, 132–136]

The injection pressure causes flow induced stresses to the plastic part according to figure 9. The polymer chains are stretched and oriented to flow direction during the injection phase. The cooling begins from the outer layer due to the contact with the cooled mold wall and due to the cooling, the polymers chains begin to relax. As the inner layer cools down slower, the unrelaxed polymer chains of the inner layer restrict the relaxation of the outer layer polymer chains. This causes tensile residual stress (T) to the outer layer and compressive residual stress (C) to the inner layer of the plastic part.

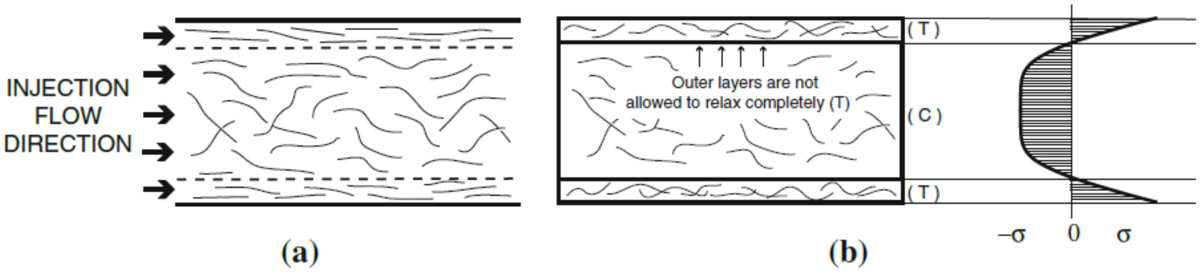


Figure 9. The formation of flow induced stresses due to injection pressure (Guevara-Morales & Figueroa-López, 2014).

The packing pressure “forces” the plastic to stay compressed in the mold during the cooling time. The formation of the flow induced stresses during packing are presented in the figure 10. If the packing pressure is low (a), there is practically no pressure in the inner layer during the cooling phase, and the volume in the core layer reduces, which causes compressive stresses (C) to outer layer and tensile stresses (T) to the core layer of the injection molded part. In case of high packing pressure (Fig. 10b), the pressure in the core area remains high and the residual stress distribution is similar to the injection pressure phase presented in the figure 9 with tensile outer layer and compressive core. In the figure 10c the stress distribution is more complex with tensile (T) outer layer and core layer, but compressive (C) middle layer in between. This kind of stress profile could result from packing pressure profile, where the pressure in the inner layer falls to zero in the end of the packing phase, when thicker outer layer has cooled down. Flow induced stresses are often neglected in computer simulation models, as these stresses have least effect on the end product properties (Fan;Yu;Zuo;& Speight, 2017).

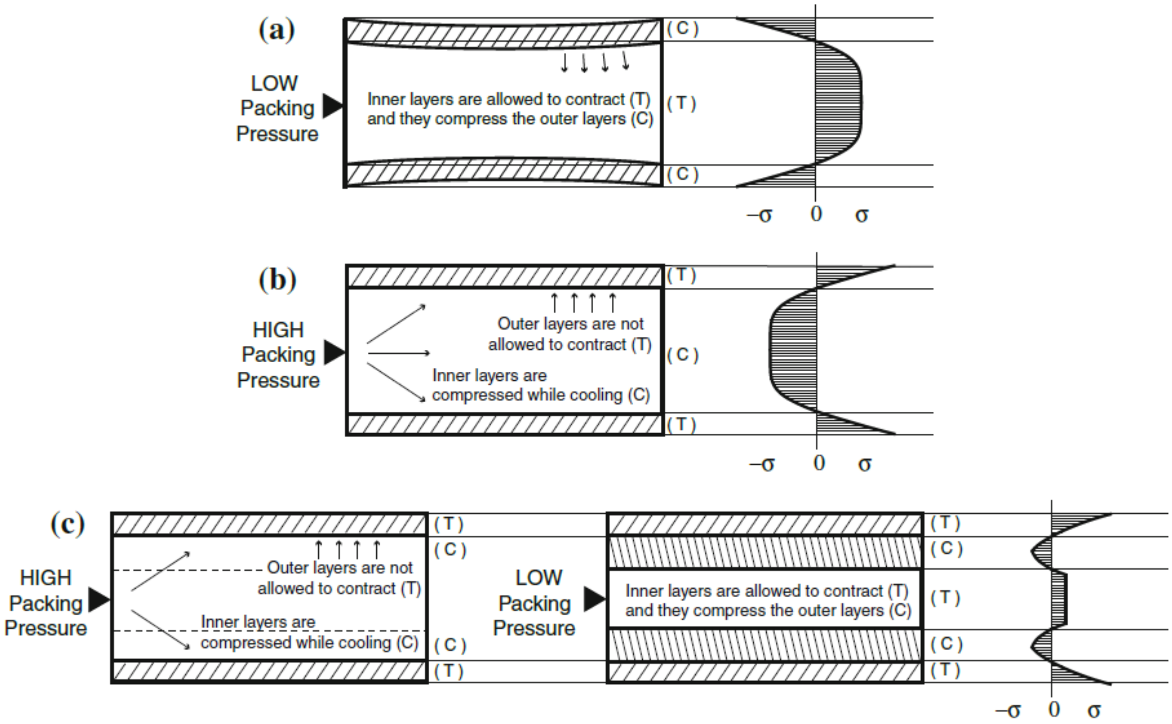


Figure 10. The formation of flow-induced stresses due to packing pressure (Guevara-Morales & Figueroa-López, 2014).

If the cooling is uneven, for example, because of the temperature differences within the mold, the shrinkage is uneven and residual stresses occur. These are called thermally induced stresses. As the cooling is basically always uneven when it comes to plastics, due to the gradual filling of the cooled mold cavity, poor thermal conductivity of plastic material and differences in the parts wall thickness, there will always be some residual stresses caused by this. In some cases these stresses cause visual warpage, if the polymer material and the part design are prone to deform. The formation of thermally induced stresses are presented in the figure 11. The polymer temperature is presented as a curve in the left side of the figure. T_{freeze} presents the temperature, where the polymer solidifies. The stress curve on the right side presents the formation of compressive (C) and tensile (T) stresses during the cooling. The relationship between warpage and thermally induced residual stresses are presented in the figure 12. (Guevara-Morales & Figueroa-López, 2014.) (Koslowski & Bonten, 2017.) (Macías;Meza;& Pérez, 2015.)

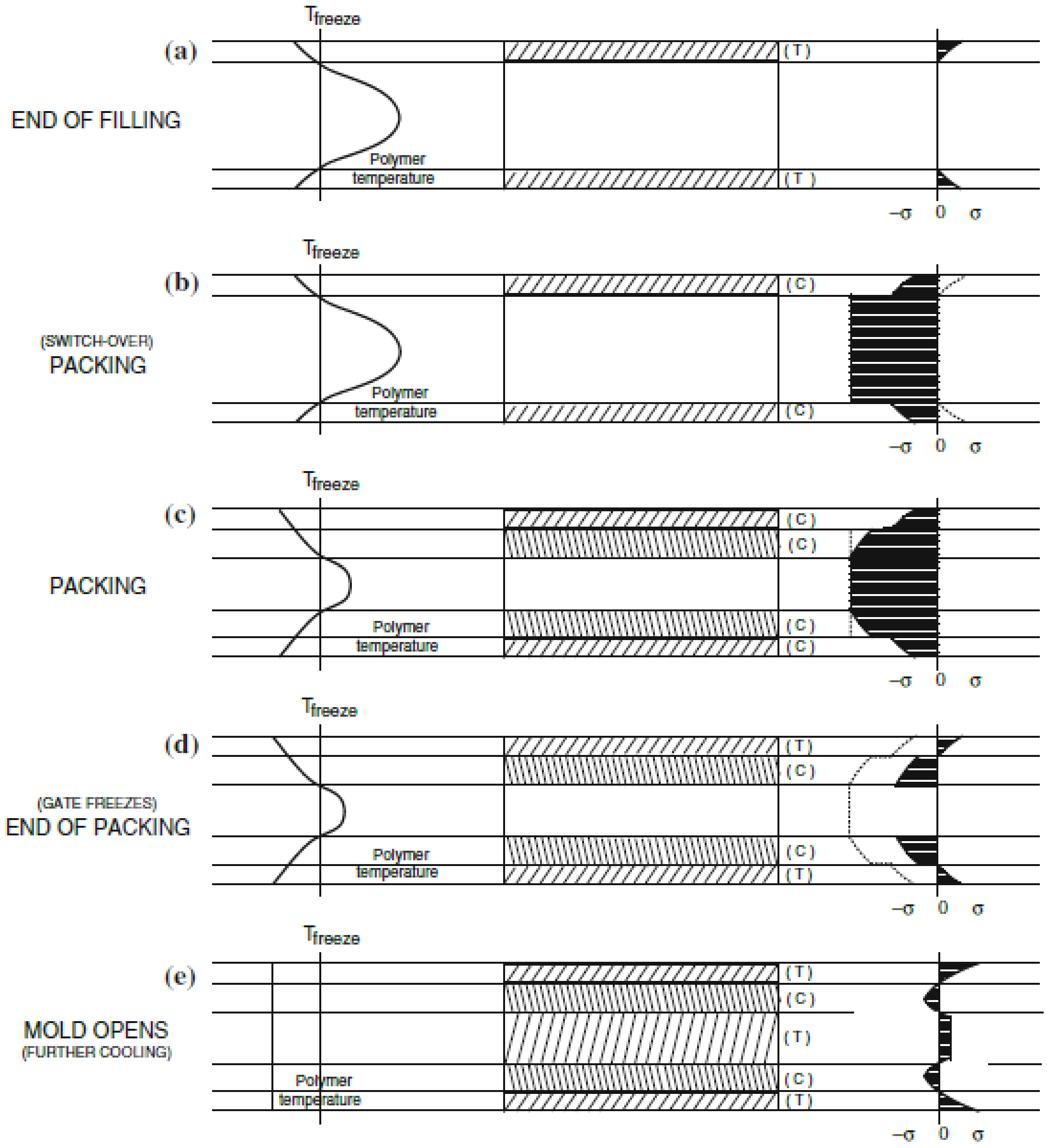


Figure 11. The formation of thermally induced stresses during injection molding (Guevara-Morales & Figueroa-López, 2014).

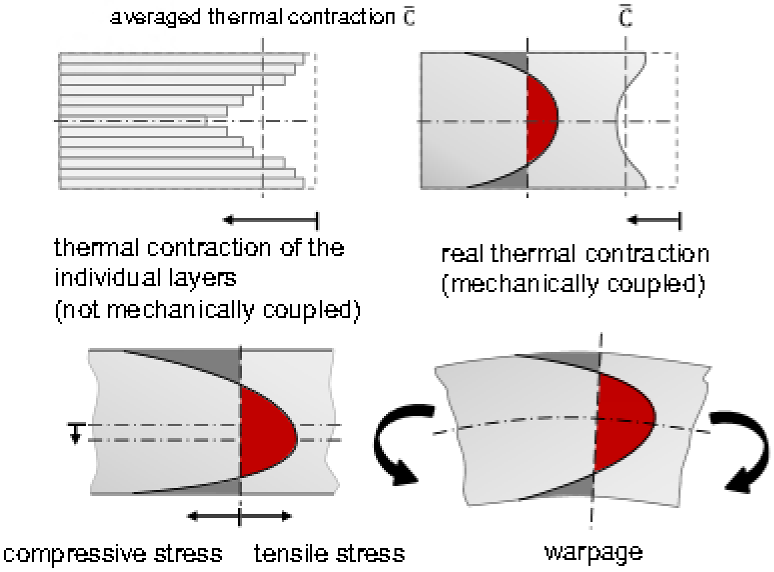


Figure 12. Residual stress and warpage in the cooling phase (Koslowski & Bonten, 2017).

Mold cooling in injection molding is done with a water or oil circulation system. The medium is tempered to a specific temperature according to the utilized plastic. The optimal mold temperature is most often stated in the product data sheet of the utilized material, provided by the material manufacturer. According to Kerkstra & Brammer (2018), the factors that affect to optimized and stabile mold tempering are turbulent flow, optimized circulation and the heat transfer efficiency of the tooling materials. So basically the main effect of efficient cooling comes from the mold design phase. In processing phase it is important to make sure, that the flow of the medium is optimized, and the temperatures are set correctly. (Kerkstra & Brammer, 2018, pp. 125-131.) (Karthikeyan;Jayabal;Kalyanasundaram;& Boopathi, 2015.)

According to ASTM D7474-17 (2017) injection molded parts with residual stress level below 6 MPa to 8 MPa are concidered to be well-molded. For this reason, the level of residual stresses should not be approved to be higher than 8 MPa even before the annealing, as this could refer to unoptimized injection molding process.

2.4 The effect of mold and part design on residual stresses

Kamal;Lai-Fook;& Hernandez- Aquilar (2002) presents that the design of the plastic part and the mold has an effect to the residual stresses of injection molded parts due to mechanical restriction of the mold (Kamal;Lai-Fook;& Hernandez- Aquilar, 2002). Variation on the wall thickness of the injection molded part causes variation in the cooling time and so has an effect on the level of residual stresses. Nowadays, when new plastic parts are designed, the residual stress level is often evaluated utilizing computer-aided engineering (CAE) analysis. These calculations are comparable between different designs, but they do not usually predict the actual level of residual stresses in a finished product accurately due to the fact that some of the variables are neglected or evaluated incorrectly. Still, the high stress areas can be evaluated in the analysis. In the figure 13 it can be detected that flanges and other areas with thicker wall are prone to higher residual stress level. (Muniesa;Clavería;Javierre;Elduque;& Fernández, 2017.)

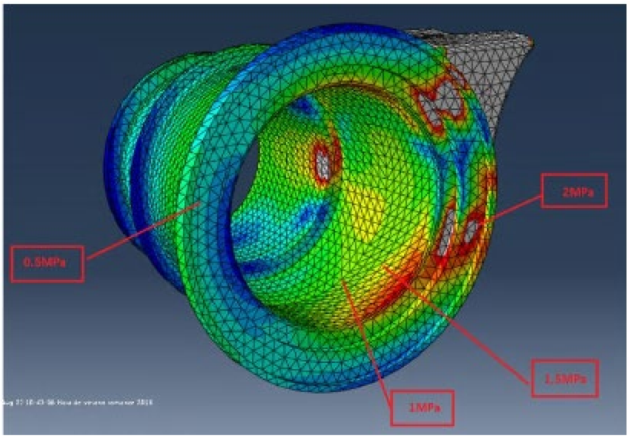


Figure 13. An example of the effect of the wall thickness to residual stress distribution in an injection molded part (Muniesa;Clavería;Javierre;Elduque;& Fernández, 2017).

One significant part of the plastic product design, that has an effect on the level of residual stress is the location, shape and size of the injection channel and the gate (Koslowski & Bonten, 2017) (Xie;Guo;Jiao;Ding;& Yang, 2014). The injection point area is typically considered a high stress area in injection molded parts. In the figure 14 an example is presented of stress level in the injection area. (Muniesa;Clavería;Javierre;Elduque;& Fernández, 2017.) According to Guevara-Morales & Figueroa-López (2014) the channel design is less significant in formation of residual stresses than the processing conditions. Xie;Guo;Jiao;Ding;& Yang (2014) concluded that the gate size effects significantly to the flow rate, and therefore to the level of residual stresses. It has been notices in practice that parts that are manufactured utilizing a hot runner system have lower level of residual stresses, than those manufactured utilising traditional cold runner molds. (Xie;Guo;Jiao;Ding;& Yang, 2014.)

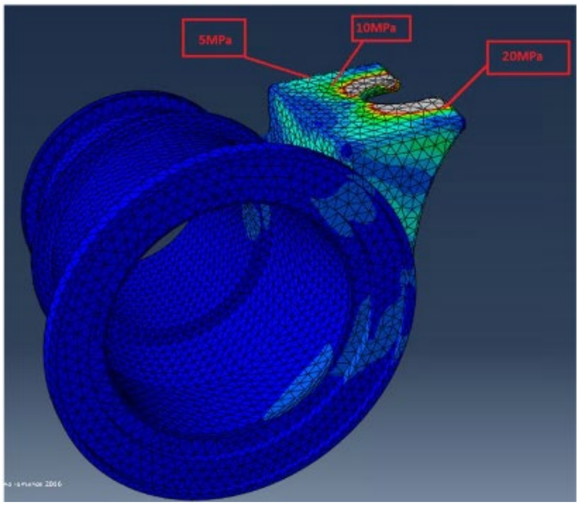


Figure 14. An example of residual stress concentrated in the injection area. (Muniesa;Clavería;Javierre;Elduque;& Fernández, 2017).

Polymer chain relaxation and the restrictions of this relaxation appears to be the root cause for the formation of residual stresses in injection molding process. The restrictions are caused by the mold and the less oriented polymer chains in the inner layers. By optimizing the injection molding process parameters, the level of residual stresses can and should be reduced to a level of 8MPa or below. In the mold design phase the designer has probably not much to say about the shape of the product. In order to control the level of the residual stresses in the finished product, the mold designer should optimize the design of the cooling channels inside the mold and cores, and select the mold and core material in order to optimize the thermal conductivity to improve cooling and temperature stability.

3 MATERIAL PROPERTIES OF POLYPHENYLSULFONE

In this chapter the thermal properties of the PPSU are presented in order to find out the parameters that can be tested in the annealing process. Also other properties are presented in order to understand the behavior and performance of PPSU compared to other amorphous thermoplastics.

Polyphenylsulfone (PPSU) is a high-performance sulphone polymer, which can remain its impact strength properties in high temperatures. Other sulphone plastics are in example polysulphone (PSU) , PESU and PPSE. PPSU is an amorphous thermoplastic polymer. This means that PPSU is in solid state below its glass transition temperature [T_g], and above it PPSU behaves like a viscous liquid. As an amorphous polymer, PPSU has an unorganized molecular structure in solid state. Thermoplastics can be reprocessed multiple times, so PPSU can be re-grinded and re-processed. (Yang, Chen, Lu, & Gao, 2016.) PPSU has an exceptionally good resistance to chemicals. (BASF, 2019) (Solvay Specialty Polymers, 2014). As PPSU is an expensive, high-performance plastic, it has only few manufacturers and not too many commercial grades (Glenz, 2007). Some of the most significant properties of PPSU are presented in this chapter.

3.1 Chemical properties

As the polymer name, polyphenylsulfone, suggests, the chemical structure of PPSU contains phenyl rings and also Sulfur in sulfonyl functional group. In the figure 15, the molecular model of PPSU is presented.

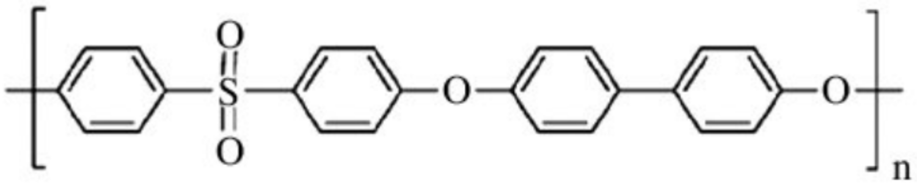


Figure 15. The molecular structure of PPSU (Sani;Lau;& Ismail, 2014).

PPSU provides the best environmental stress crack resistance (ESCR) of the sulfone polymers, as it has excellent resistance to most acids, bases and alcohols. PPSU is only partly resistant or non-resistant to aromatic hydrocarbons and ketones, such as methyl ethyl ketone (Solvay Specialty Polymers, 2019.)

3.2 Physical properties and processing conditions

PPSU is a hygroscopic plastic, so it should be dried before processing. In drying, even as high as 177°C temperatures can be utilized. T_g is 215-225°C depending on the grade (BASF, 2019) (Solvay Specialty Polymers, 2019).

Maximum melt temperature in injection molding is 395°C. Mold temperature can be adjusted between 138-160°C.

3.3 Mechanical properties

The mechanical properties of two different PPSU grades are presented in the table 2.

Table 2. The mechanical properties of PPSU (BASF, 2019) (Solvay Specialty Polymers, 2019).

	Tensile strength [MPa]	**Tensile Modulus [MPa]**	**Tensile strain at yield [%]**	**Impact strength, nothed, Izod [kJ/m^2]**	**Density [g/cm^3]**
Solvay Radel	75	2421	7.0	7.5	1.31
BASF Ultrason	85	2650	6.9	8	1.37

3.4 The effect of residual stresses to material properties of PPSU

The residual stress level has a significant effect on the chemical endurance of PPSU material as the ESCR decreases. This also applies to external stress. Whenever the PPSU part is under mechanical stress its chemical endurance diminishes, whether the stress is external or internal. Hense, the residual stresses can have a positive effect on mechanical properties of PPSU material. Tensile strenght has been proven to be higher on amorphous thermoplastic products that have compressive residual stresses in the part surface. Hornberger;Fan;& DeVries (1986) noticed that these stresses can significantly increase the impact strenght and tensile properties of polycarbonate. This theory could be applicable for PPSU as it has similar material properties as polycarbonate. (Hornberger;Fan;& DeVries, 1986.) (Solvay Specialty Polymers, 2019.)

In this chapter the properties of PPSU was presented. Based on these properties, the possible annealing parameters can be determined. As the T_g of the PPSU is 215-225°C, the annealing temperature should be lower, so the fitting does not change its shape during the process. The mold temperature is between 138-160°C, so the annealing temperature should be higher or at least as high in order to achieve relaxation in the polymer chains. As the drying temperature is as high as 177°C, a relaxation of the residual stresses is not expected to occur below this temperature. Still the effects on mechanical and chemical properties are examined from 135°C to 210°C in order to increase knowledge of the behavior of PPSU.

4 PLASTIC FITTINGS

As this research focuses on the annealing of PPSU fittings, the main characteristics and product requirements are presented in this chapter. The purpose of fittings is to connect water pipelines utilized in technical building solutions in a leak-proof and reliable manner, to enable the connection between different pipe sizes, and enable the branching of the pipeline. Metal has been traditionally used as a material for these fittings, mainly brass due to its corrosion resistance. However, the expensive price of brass and the limited availability have guided the manufacturers in research for alternative materials. Plastics have been used in the past decades to replace other materials, and in the fittings manufacturing, plastics, such as PPSU has become an alternative to metal (Biron, 2013, pp. 124-125). In this chapter the requirements for the plastic fitting properties are presented in order to define the quality standard for the annealed PPSU fittings.

4.1 Chemical requirements

It is mainly assumed that only water is transported inside the potable water pipelines, although the water is not always clean. However, various chemicals, such as acetone, may be used in the pipeline installation phase to clear the pipe markings from the visible parts. Different greases, lubricants, adhesives and sealants may also be used in the joints and threads. Various chemicals, such as chlorine-containing cleaners or strong bases, may also be used for internal line cleaning. Due to these factors, the pipelines should be chemically inert and have adequate resistant to chemical stress. The PPSU fittings are also utilized in radiant heating pipelines, where different kinds of cleaners and antifreeze chemicals are utilized. The fittings can also be subjected to various building materials, such as insulation foams, paints, plasters and so forth. (Uponor Suomi Oy, 2019.)

4.2 Mechanical requirements

In the fittings, the mechanical stress is particularly applied to the corners and to thin walled parts, such as sealing grooves. The pressure inside the pipeline, and especially the pressure variations, cause dynamic stress on the inner walls of the fitting. Thermal expansion due to thermal changes causes dynamic stress, especially to the corner area. In particular, during the pipeline installation phase, they are subjected to static mechanical stress such as bending and compression. Depending on the accuracy of the installation, there may be various stresses in the pipeline that may eventually lead to a breakage. Breakage of the fitting can result in major water damage or, in the case of latent leakage, even hidden moisture damage and mold in the property. In product development and design, sufficient safety factors must be taken into account in order for the product to withstand the requirements through its lifetime. In quality control pressure tests, the fittings must withstand an internal pressure of at least four times the operating pressure. The service life of the pipeline is 50 years. In aging tests, the fitting must withstand the lifespan twice. (ISO 15875, 2002.) (Uponor Suomi Oy, 2019.)

4.3 Dimensional requirements

As the fittings purpose is to provide leak-proof connections between pipes, the tolerances for the fittings critical dimensions are tight. The fitting should fit inside the corresponding pipe with moderate effort, and the sealing surfaces should provide a pressure proof connection. The wall thickness of the fittings should be adequate to gain the required mechanical properties, but thin enough to provide optimal flow characteristics.

4.4 Other requirements

As the fittings are utilized in potable water solutions, the fitting material has to be approved for usage in food applications. This means, that any chemical utilized in the manufacturing process cannot be harmful to living beings. The fittings are regularly tested by external laboratories in case of any harmful substances. Also visual characteristics are noteworthy, as in some applications the fittings are surface-mounted.

The demands for the PPSU fittings performance form a baseline to this research. The annealing method should be such, that the requirements for the fittings performance are fulfilled. Therefore chemical, physical and mechanical properties of the PPSU fitting are measured and compared in this research.

5 ANNEALING OF INJECTION MOLDED PPSU PARTS

In this chapter the principals of the annealing procedure is examined in order to find the possible annealing parameters for annealing of the PPSU fittings. The batch annealing process and the inline annealing process are described. The possible methods and equipment for inline annealing of the PPSU fittings are sought.

5.1 Principles of the annealing procedure

The objective of the annealing process is to reduce the level of residual stresses in injection molded parts. According to Solvay Specialty Polymers (2019), finished PPSU products should not have more than 4 MPa of residual stresses. As the product is considered to be well-molded, when the stress level is 8MPa or below, annealing is performed in order to reduce the stress level to 4 MPa or below. (ASTM D7474-17, 2017.) (Solvay Specialty Polymers, 2019.) In the figure 16 the reductive effect of annealing to residual stress level is presented. Kim;Kim;Pak;& Youn (2012) studied the effect of infrared radiation annealing on the level of residual stresses of injection molded polycarbonate TV bezels. The level of residual stresses was determined utilizing a hole drilling method, so the results are presented in different depths measured from the part surface. The reductive effect on the residual stresses is the most efficient near the part surface as seen in the figure 16.

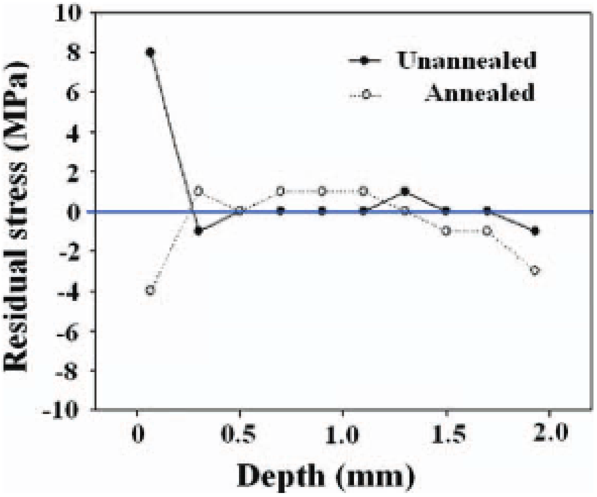
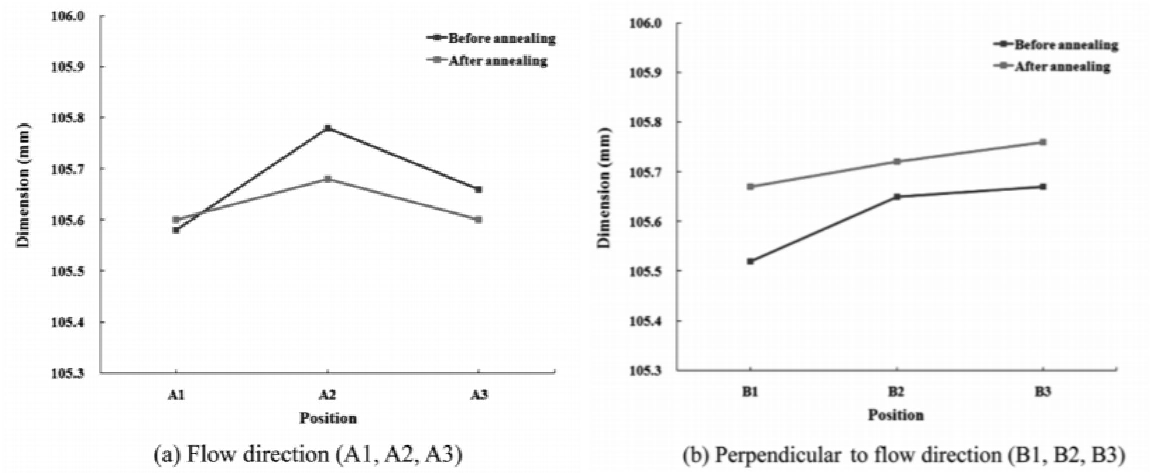


Figure 16. The effects of infrared annealing to the level of residual stress on injection molded polycarbonate TV bezel. The residual stress level is measured by the hole drilling method from different depths from the part surface. (Kim;Kim;Pak;& Youn, 2012).

In annealing, the injection molded PPSU fittings are heated to pre-determined temperature for a determined time in order to allow the molecular chains to relax. This means that the utilized temperature should be near the T_g of the polymer material. The temperature should not be equal or above the T_g, as the product might change its shape during annealing. (Kim;Kim;Pak;& Youn, 2012.) Cho;Park Seo;Kim;& Lyu (2012) proved dimensional changes due to annealing in different positions of a test part according to figure 17 a and b. The measurement point A1-A3 and B1-B3 are presented in the figure 18. (Cho;Park Seo;Kim;& Lyu, 2012.) The time needed to achieve the relaxation of the polymer chains is dependent on the wall thickness of the product, thermal conductivity of the item material, thermal conductivity of the media and of course the utilized temperature according to experience and prior internal studies.



(a) Flow direction (A1, A2, A3)

(b) Perpendicular to flow direction (B1, B2, B3)

Figure 17 a and b. Example of dimensional changes due to annealing (Cho;Park Seo;Kim;& Lyu, 2012).

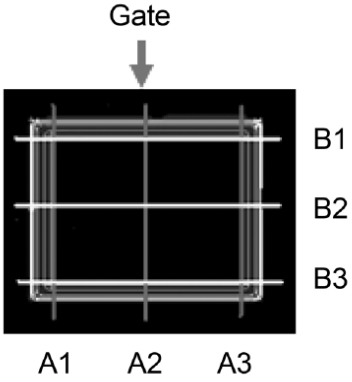


Figure 18. Measurement points A1-A3 and B1-B3 (Cho;Park Seo;Kim;& Lyu, 2012).

5.2 Batch annealing

In batch annealing a large amount of products are annealed at a time, usually in an industrial convection oven. The process parameters, time and temperature, are adjusted based on the material properties, the shape, size and amount of items and how they are laid out in the oven.

At the target company the current batch annealing method is developed to be easy, safe and reliable. The fittings are collected to steel containers, which have ventilating ducts to improve the air circulation in the central part of the container. The full containers are put into a room temperature oven, four containers at the time. The temperature is set to rise at 190°C and the annealing time is set at 10 hours. It has been measured that it take approximately 4 hours for the temperature to rise at 190°C in the middle parts of the container.

Annealing time of 1 hour at 195°C is recommended for PPSU (Solvay Specialty Polymers, 2019), but according to experience the lower temperature and longer time diminishes the risk for shape and dimensional changes and ensures the annealing effect throughout the batch. At the target company the annealing is usually done during unstaffed nightshift, so in labor point of view it would not matter if the length of the process would be shorter as the oven would anyway be emptied during the morning shift. In the efficiency point of view, the optimal annealing time would be seven hours, so one annealing batch could be handled per shift.

5.3 Inline annealing

In inline annealing method the plastic parts are heated in a conveyor belt type of annealing oven straight from the injection molding machine. This means that even though the parts are still warm from the molding, the annealing procedure should be efficient enough to reduce the residual stress level adequately in a limited time period. In in-line annealing method the mass of the products is lower, so the heat does not have to pass through multiple layers of products, as in batch annealing process. Typically infrared or gas catalytic infrared is utilized as a heat source, as the infrared radiation distributes the heat more evenly throughout the treated part. In-line type infrared ovens are presented in the figures 19 and 20. (Trimac Industrial Systems, 2019.) (INTEK Corporation, 2019.)

Figure 19. Plastic annealing infrared oven (Trimac Industrial Systems, 2019).

Figure 20. Continuous custom annealing infrared oven (INTEK Corporation, 2019).

The difference between batch annealing and inline annealing is that in inline annealing the treated items travel through the heater system straight from the injection molding machine, without cooling to room temperature after molding. In inline annealing the most common heat source is infrared, but in batch methods convection ovens are utilized. The inline annealing can be simulated utilizing a laboratory size infrared oven and treating small amount of fittings at a time.

6 DEFINING THE RESIDUAL STRESS LEVEL OF INJECTION MOLDED PPSU FITTINGS

In this research the residual stress level is evaluated by utilizing chemical testing based on environmental stress cracking caused by residual stresses in injection molded PPSU products. The testing is done utilizing a method that is simplified from two chemical testing methods, which are ASTM D7474-17 and testing instructions provided by Solvay polymers. In this chapter these chemical testing methods are described.

The chemical testing method is selected as is provides adequate level of accuracy of the level of residual stresses in order to reach the goals of this project. In order to achieve the certain level of stresses, it is not compulsory to find out the exact level of residual stresses or to determine the distribution of the stresses. The simplified version of the chemical testing method (MEK-test) has been utilized daily at the target company´s production unit in quality assurance to verify the effectivity of the batch annealing.

6.1 Determining the level of residual stresses according to ASTM D7474-17

The ASTM D7474-17 method is based on exposing the finished plastic parts to series of chemical reagents which cause cracking and/or crazing of sulfone plastics. An example of cracking is presented in the figure 21. Cracking and crazing is analyzed visually without the help of optical devices (excluding glasses) from the surface of the sample. Color changes in the part surface are not considered as crazing or cracking.

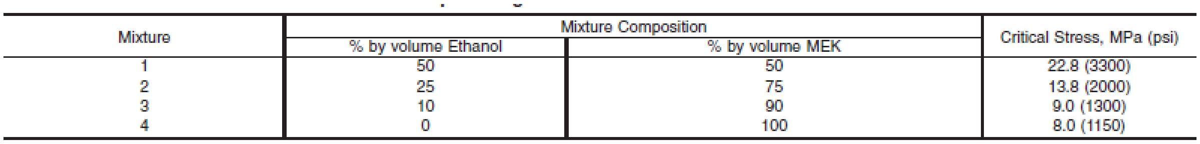
Figure 21. An example of cracking in the PPSU fittings flange in chemical testing.

Samples are collected and conditioned in room temperature for minimum of 4 hours before testing. The conditioning is not compulsory, but recommended in a case of controlled study. Due to practicality and comparability of the results, the conditioning of 24h is performed in this study. It is practical to perform the tests on the next workday instead of i.e. four hours after sampling. (ASTM D7474-17, 2017.)

The utilized solvents are dozed into glass containers. In between testing, the containers are closed in order to prevent the solvents from vaporizing, as this may cause variation in the results as the percentage of the solvents change. All tests are done with fresh solvent mixtures. (ASTM D7474-17, 2017.)

The samples are rinsed clean with isopropyl alcohol and dried in air. Dry and clean samples are soaked in to the solvent mixture which indicates the highest level of residual stresses for one minute and then rinsed with water. The sample is dried and visually inspected. If cracking or crazing is detected, the test is not continued, but the level of residual stresses is stated to be higher than the limit value. If no crazing is detected in the sample, it is soaked to the next solvent mixture for one minute, rinsed with water and examined for crazing. This procedure is continued until cracking or crazing is detected, and the level of residual stresses is determined. In the table 3, the formula of the solvent mixtures and the corresponding level of residual stresses is presented for PPSU. (ASTM D7474-17, 2017.) The one minute time is measured with a stopwatch from when the sample is totally recessed in to the solvent to the moment when the sample is removed from the solvent. The sample is rinsed with clean water immediately after it is taken out from the solvent. This procedure is repeated for all the tested samples.

Table 3. Solvent mixtures and corresponding level of residual stresses for PPSU according to ASTM D7474-17 (ASTM D7474-17, 2017).



Mixture	Mixture Composition		Critical Stress, MPa (psi)
	% by volume Ethanol	% by volume MEK	
1	50	50	22.8 (3300)
2	25	75	13.8 (2000)
3	10	90	9.0 (1300)
4	0	100	8.0 (1150)

6.2 Solvay method for determining the level of residual stresses for PPSU

The bases of this testing method are the same as in ASTM D7474-17 method, but the solvents are tailored for a certain sulfone plastic grade.

The different level of residual stresses is based on the time the sample is dipped into the solvent. The corresponding time and level of residual stresses are presented in table 4. In this method the samples are also washed and rinsed with isopropyl alcohol before testing.

Table 4. Test time, chemical and corresponding level of residual stresses in Solvay -method for PPSU (Solvay Specialty Polymers, 2019).

Stress (Mpa)	**Chemical/exposure time**	
	1 min	**3min**
12	Ethyl Acetate	
10		Acetone
8	MEK	
7		90% MEK + 10% Isopropanol
5	5 % N. Methyl Pyrrolidone + 95% MEK	
2		MEK

6.3 MEK-testing in quality control of the PPSU products

The target company's MEK-test in quality control is a simplified test method from of the ASTM D7474-17 and the Solvay method in order to make it usable in everyday testing in the production quality assurance. The difference in this method is that only pure MEK-solvent is utilized. The level of residual stresses is determined via the time of the exposure to the chemical (30s / 1min / 2min / 3min). The test time and according level of residual stress is presented in the figure 22.

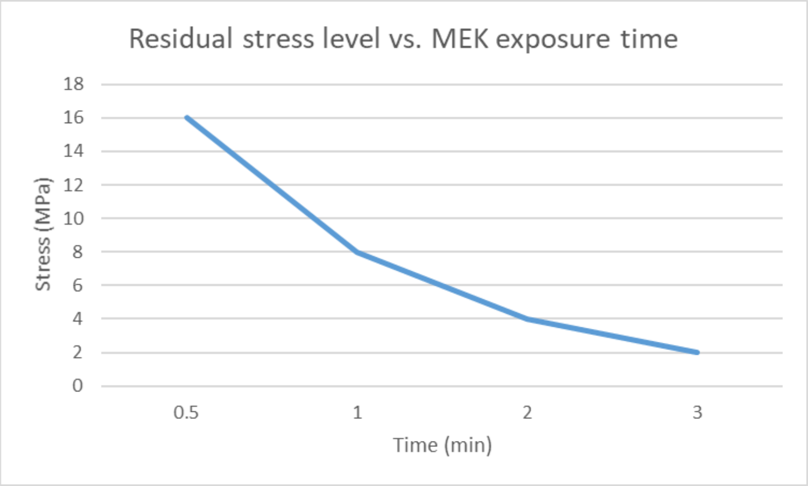


Figure 22. MEK-test: residual stress level in relation to MEK exposure time.

Pure methyl ethyl ketone does not change its composition as time passes, even though it vaporizes. Still, the solution may lose its efficiency, if it absorbs water from air. For this reason the methyl ethyl ketone is renewed weekly for production quality assurance testing.

6.4 Other methods

The residual stress level can be analyzed more specifically in various methods. The most utilized method is hole drilling strain-gage method according to ASTM E837-13a. Other strain gage methods are widely utilized based on literature review. (Fan;Yu;Zuo;& Speight, 2017.) (Guevara-Morales & Figueroa-López, 2014.) In this research the hole drilling method was not utilized, because the complicated shape of the products under investigation and the lack of prior researches where the method has been utilized for such parts made of PPSU.

When determining the residual stress level for transparent plastic components, also birefringence measurement and analysis is utilized (Adhikari;Bourgade;& Asundi, 2016) (Cho;Park Seo;Kim;& Lyu, 2012). An example of birefringence measurement arrangement is presented in the figure 23 (Cho;Park Seo;Kim;& Lyu, 2012). Macías;Meza;& Pérez (2015) compared the firebringence analysis and chemical attack experiments for plastic cover lens. According to their research, these two methods gave similar residual stress level results, even though chemical attack experiment gave slightly higher stress levels than the photoelacticity experiment. In the figure 24 the comparison result are presented. (Macías;Meza;& Pérez, 2015.)

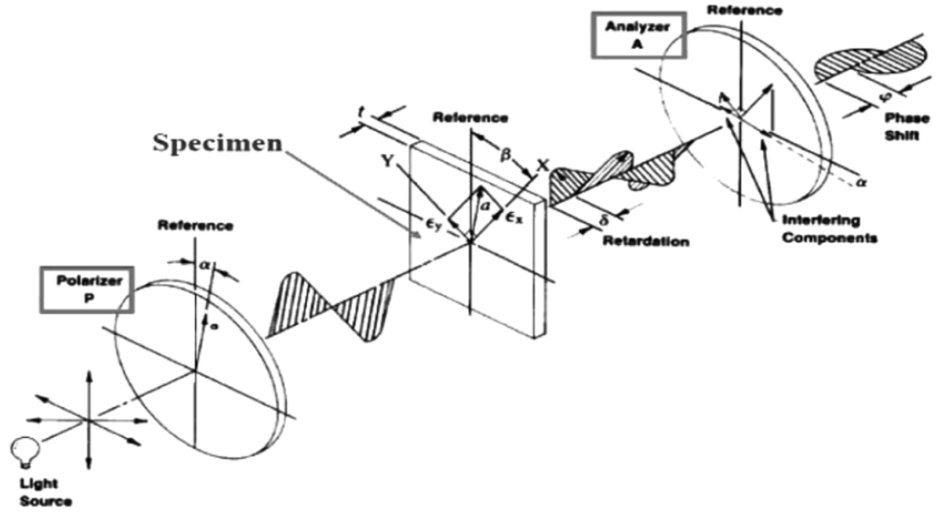


Figure 23. Principal of birefringence polariscope utilized in determining the residual stresses from transparent plastic components (Cho;Park Seo;Kim;& Lyu, 2012).

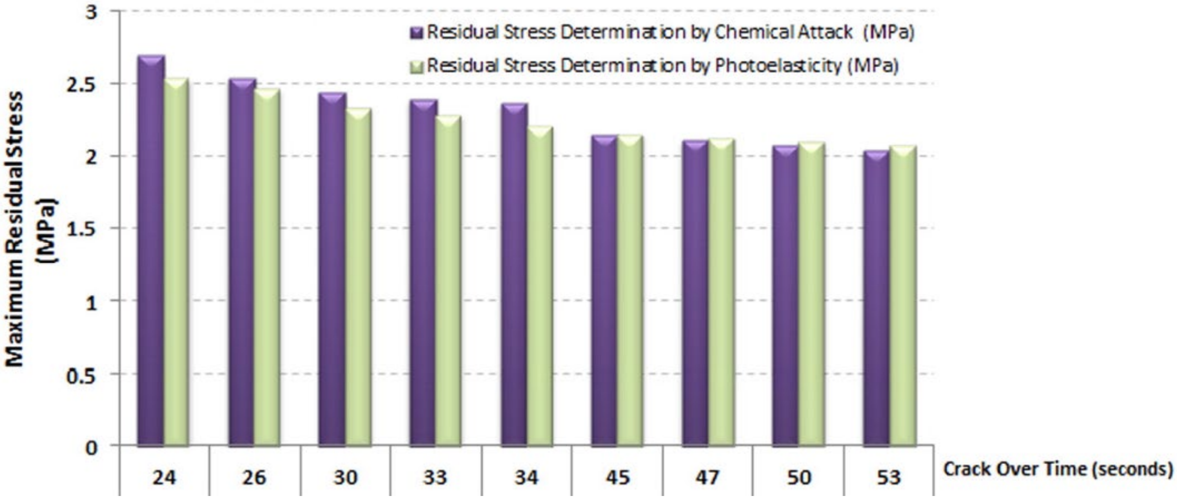


Figure 24. Comparison between birefringence and chemical analysis (Macías;Meza;& Pérez, 2015).

In this chapter it was stated, that the MEK-test has been utilized in the production of the target company as a quality control method for annealing. Based on the literature review this method is developed according to ASTM D7474-17 and information received from PPSU manufacturer. As the target company has a long time experience of MEK-testing, it is justified to utilize this testing method also in this research. As there is no experience or equipment for the hole drilling method, nor the PPSU fittings are transparent and so suitable for the birefringence method, the residual stress level is determined utilizing only the chemical attack method in the experiment part of this research.

7 EXPERIMENTS

In order to find out if the PPSU fitting can be annealed utilizing an inline annealing method, the fastest way to reduce residual stresses to desired level should be determined. Because there is limited time to transport the fitting from the injection molding machine to a packing cell, and the fitting should also have time to cool down before packing, the annealing time should be optimized. Still, the quality of the process should not be compromised. In this chapter the practical experiments are presented in order to find the shortest annealing time possible to achieve the optimal product quality.

The PPSU fittings annealed utilizing in-line annealing method should have equal quality level as the PPSU fittings annealed with the current batch annealing method in chemical endurance, mechanical properties and dimensional stability. In order to define the quality of the current method the following tests are performed to as molded samples and annealed samples:

- Chemical testing utilizing 2 minute MEK-test (simplified method of the ASTM-D7474-17).
- Mechanical testing: The maximum bending stress [MPa] of the annealed and as molded fittings is determined and compared.
- Dimensional measurements: Weight, length and diameter of the annealed and as molded PPSU fitting is measured and compared.

7.1 Comparing and verifying the chemical testing methods

In order to verify the chemical testing method and modifying it to be suitable for finding out specified residual stress levels, the ASTM D7474-17, chemical test by Solvay and MEK-test are compared. The full testing scale is presented in table 5. This test proved that the cracking and crazing of the samples increased according to the strength of the applied chemical and time in all steps of ASTM and Solvay tests. This test also showed that 100% MEK does not give reliable result with testing time less than 1 minute. The samples soaked in 100% MEK for 30 seconds showed more color changes and crazing that the samples soaked in acetone for 3 minutes. The N-Methyl Pyrrolidone + MEK mixture was not tested.

Table 5. Chemical test method verification.

	ASTM*	Uponor	ASTM*	Solvay	Solvay	ASTM*	ASTM*	Solvay	Solvay	Uponor	Solvay
	Mixture 1		Mixture 2			Mixture 3	Mixture 4				
Mpa	22.8	16	13.8	12	10	9	8	7	5	4	2
Reagent	MEK50%+ Ethanol 50%	MEK 100%	MEK75%+ Ethanol 25%	Ethyl acetate	Acetone	MEK 90%+ Ethanol 10%	MEK100%	MEK W-90%+ Isopropanol 10%	N-Methyl Pyrrolidone 5%+ MEK W-95%	MEK	MEK
Time	1min	30s	1min	1min	3min	1min	1min	3min	1 min	2min	3min
Color changes/crazing	-	++	-	-	+	++	+++	++++	NA	+++++	++++++

7.2 Sampling

The PPSU fitting chosen for developing the new annealing method was chosen on the following bases:

- The residual stress level of as molded samples is between 10 MPa and 8 MPa.
- The samples are suitable for bending test without required additional equipment.
- The item is one of the most produced items.
- The mold has 4 cavities.

7.3 Defining the level of residual stresses of the as-molded samples

In order to select a suitable PPSU fitting utilized in the testing, the residual stress level of the selected fitting was verified. Samples were collected randomly from normal production.

The approximate residual stress level of the as molded samples is performed with following procedure:

1. Samples are rinsed with isopropyl alcohol and air dried.
2. As molded samples are soaked into acetone for 3 minutes, rinsed with water, dried and visually checked for cracks. (10 MPa level)
3. The undamaged samples are soaked into MEK for 1 minute and visually checked. (8MPa level)

The level of residual stresses is stated based on the level where more than 5% of the samples show cracking. This rules out random variation and the results are based on normal quality levels minimum performance. Color changes are not considered as cracking/crazing. The result is stated OK if no cracks can be detected on the surface of the fitting in visual inspection. Flash light is utilized to improve the visibility of the possible cracks. In unclear cases the possible cracking is verified in microscope examination or with endoscope. As molded samples are tested to have residual stress level between 10 MPa to 8 MPa.

7.4 Determining the parameters for in-line annealing

In order to determine the optimized time and temperature combination for in-line annealing, practical testing is utilized. The basic idea of the in-line annealing is, that the PPSU fitting will be placed on conveyor belt system straight from the injection molding machine. During the transportation phase the parts are heated in a certain temperature for a certain time in order to achieve a desired level of residual stresses. In this case the desired residual stress level is equal or less than 4MPa as this is the approval limit for current process.

As there is no need to build up an actual conveyor belt system for determining the required annealing time and temperature for testing purposes, a simple infrared oven is utilized in the practical tests. The samples are put straight from the injection molding machine (within 30 seconds from ejection) to infrared oven for testing temperature and time. The temperature in the oven is measured with Fluke thermometer and the time is measured with a stopwatch. After the annealing, the samples are cooled down in air at the room temperature, or in cold water. The tested parameters are presented in the table 6.

Table 6. The tested inline annealing parameters

Cooling media	Annealing temperature	Annealing time
Air	135°C	15 minutes 30 minutes
	150°C	15 minutes
	190°C	5 minutes
		10 minutes 15 minutes 30 minutes
	200°C	5 minutes
Water		5minutes
Air	205°C	5 minutes
	210°C	5 minutes

7.5 Defining the level of residual stresses of the annealed samples with MEK-test

The maximum residual stress level of the annealed samples is tested according to the following procedure:

1. Samples are rinsed with isopropyl alcohol and air dried.
2. The samples are soaked into MEK for 2 minutes and visually checked. (4 MPa level)
3. The level of residual stresses is stated based on the level where more than 5% of the samples show cracking. This rules out random variation and the results are based on normal quality levels minimum performance. Color changes are not considered as cracking/crazing. The result is stated OK if no cracks can be detected on the surface of the fitting in visual inspection. Flash light is utilized to improve the visibility of the possible cracks. In unclear cases the possible cracking is verified in microscope examination or with endoscope.

The annealed samples are to have residual stress level of 4 MPa or less.

30 samples are tested per each annealing parameters and the results are presented in the following manner:

OK (0/30 failed) =no cracking or crazing in any of the tested samples
OK (1/30 failed) = cracks or crazed detected in 1 of 30 samples (< 5%)
NOT OK (30/30 failed) = all 30 samples showed cracks and/or crazing
NOT OK (18/30 failed) = cracks or crazed detected in 18 of 30 samples (>5%)

7.6 Mechanical properties

Mechanical properties of the as-molded and annealed parts are tested with a bending test in an external testing laboratory, Muovipoli Oy. Muovipoli and the target company has been co-operating for over 15 years, and they have a long experience of the bending tests for the PPSU fittings (Muovipoli Oy, 2019). The bending test for the PPSU fittings is a modified version of a tensile test. The same test is performed for as-molded samples, batch annealed samples and inline prototype annealed samples. Maximum force [N] is recorded and the maximum bending stress [MPa] is calculated according to the following equation:

$$\sigma = F/A \tag{1}$$

In equation 1 the σ is maximum bending stress, the F is maximum force and the A is the cross section area of the fitting.

The average, standard deviation, minimum value and maximum value of bending tests results are reported and compared.

7.7 Dimensions

In order to determine the effect on dimensions per annealing method, 30 samples are collected straight from the process and annealed according to table 7. The samples are cooled down and tempered for 24 hours and measured with caliber and weighted with a laboratory scale. The results are compare to the dimensions of as-molded samples, collected at the same time from the production as the annealed samples. The batch annealed samples are annealed according to the standard production procedure in order to find out, if the large mass of the annealed products affect the dimensions of the fittings. The average value and the standard deviation of the dimensions are analyzed and compared.

Table 7. Annealing parameters for the dimensional analysis samples.

n=30
As molded
Batch annealed
Annealed 5min@200°C
Annealed 5min@200°C +quenched
Annealed 5min@210°C

7.8 Visual changes

The samples are checked visually for changes in color, shape, surface shine or other possible visual defects/changes caused by the annealing procedure. As molded sample is used as a control sample.

In the figure 25 the experimental part of the research is presented. The test matrix is presented in the table 8.

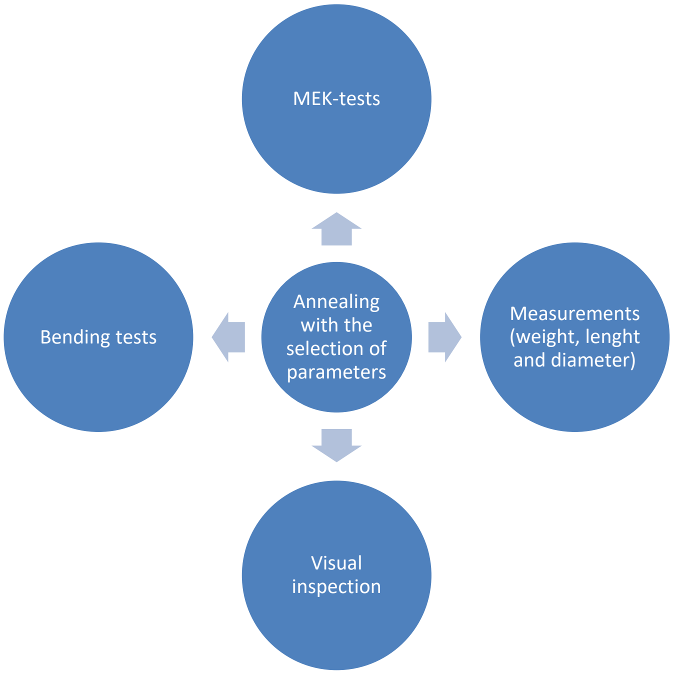


Figure 25. The different phases of the experimental part of the research.

Table 8. The test matrix.

Cooling media	Annealing temperature	Annealing time	**(MEK 2 min), n=30**	**Bending test, n=12**	**Dimensional measurements, n=30**	**Visual inspection n=30**
As molded			YES	YES	YES	YES
Air	190°C	10 h (BATCH)	YES	YES	YES	YES
	135°C	15 minutes	YES	NO	NO	NO
		30 minutes	YES	NO	NO	NO
	150°C	15 minutes	YES	NO	NO	NO
	190°C	5 minutes	YES	YES	NO	NO
		10 minutes	YES	YES	NO	NO
		15 minutes	YES	NO	NO	NO
		30 minutes	YES	NO	NO	NO
		1 h	YES	YES	NO	NO
	200°C	5 minutes	YES	YES	YES	YES
Water		5minutes	YES	YES	YES	YES
Air	205°C	5 minutes	YES	NO	NO	NO
	210°C	5 minutes	YES	NO	YES	YES

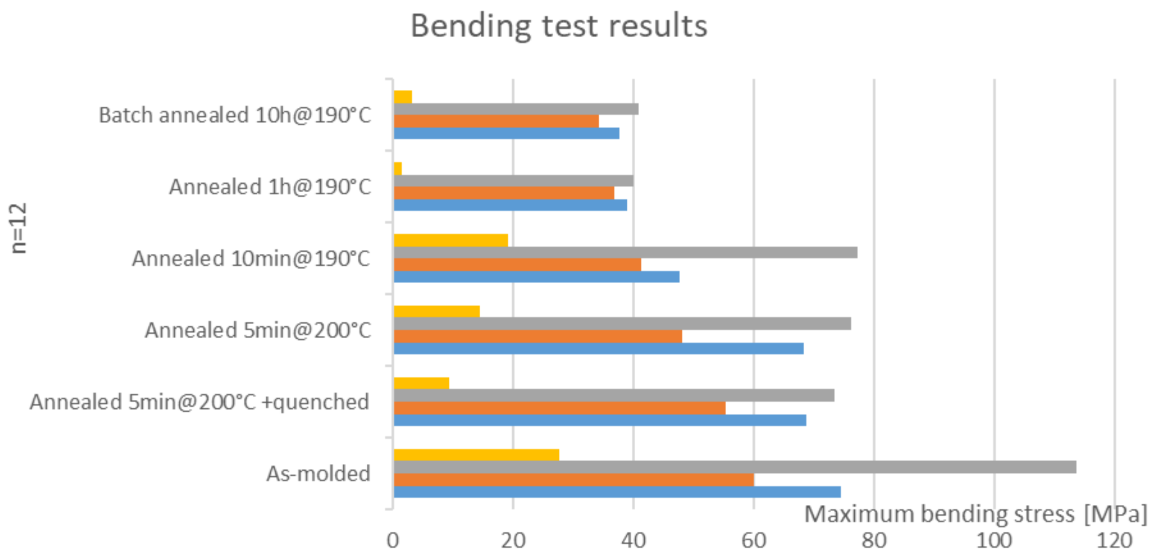
8 RESULTS

In this chapter the result of the experiments are presented. 2 minute MEK test was done in order to find out if the residual stresses obtain the level of current annealing method. The results presented in the table 9. Annealing below 190°C resulted to failure in 2 minute MEK test. In 190°C 5 minutes resulted to failure in all 30 samples, but when time was increased to 10 minutes, all samples passed the MEK-test. When temperature was raised to 200°C, annealing time of 5 minutes was enough to pass the MEK-test.

Table 9.MEK-test results.

Cooling media	Annealing temperature	Annealing time	**(MEK 2 min), n=30**
As molded			NOT OK (30/30 failed)
Air	190°C	10 h (BATCH)	OK (0/30 failed)
	135°C	15 minutes 30 minutes	NOT OK (30/30 failed)
	150°C	15 minutes	
	190°C	5 minutes	
		10 minutes 15 minutes 30 minutes 1 h	OK (0/30 failed)
	200°C	5 minutes	
Water		5minutes	
Air	205°C	5 minutes	OK (1/30 failed)
	210°C	5 minutes	OK (0/30 failed)

Comparison of mechanical test result for as-molded samples, batch annealed samples and inline annealed samples are presented in figure 26.



	As-molded	Annealed 5min@200°C +quenched	Annealed 5min@200°C	Annealed 10min@190°C	Annealed 1h@190°C	Batch annealed 10h@190°C
🟨 Standard deviation	28	9	15	19	2	3
⬜ Max	114	73	76	77	40	41
🟧 Min	60	55	48	41	37	34
🟦 Average	75	69	68	48	39	38

Figure 26. Mechanical test results.

Dimensional testing and visual check was done to five sets of samples annealed in infrared oven. The results of dimensional change analysis are presented in the tables 10 and 11. Visual changes are presented in the table 12.

Table 10. Results of the dimensional change analysis.

	Weight		Diameter		Lenght	
n=30	**Average [g]**	**Standard deviation**	**Average [mm]**	**Standard deviation**	**Average [mm]**	**Standard deviation**
As molded	15.55	0.01	20.15	0.02	11.06	0.01
Batch annealed	15.55	0.01	20.15	0.01	11.07	0.07
Annealed 5min@200°C	15.55	0.01	20.16	0.01	11.08	0.05
Annealed 5min@200°C +quenched	15.54	0.02	20.14	0.02	11.08	0.04
Annealed 5min@210°C	15.55	0.01	20.25	0.04	11.00	0.07

Table 11. The effect of the annealing parameters on physical properties of the PPSU fittings.

	Average change (%) and standard error of the mean (S)					
n=30	**Weight**	**S**	**Diameter**	**S**	**Lenght**	**S**
Batch annealed	-0.013 %	0.003	-0.02 %	0.003	0.17 %	0.002
Annealed 5min@200°C	-0.009 %	0.003	0.02 %	0.002	0.21 %	0.013
Annealed 5min@200°C +quenched	-0.064 %	0.003	-0.06 %	0.003	0.21 %	0.009
Annealed 5min@210°C	-0.015 %	0.003	0.48 %	0.003	-0.52 %	0.008

Table 12. Results of the visual inspection.

N=30	**Visual changes**
Batch annealed	No changes can be detected
Annealed 5min@200°C	The surface is slightly shinier after annealing and cooling.
Annealed 5min@200°C +quenched	The surface is slightly shinier after annealing, but the effect reduces after cooling.
Annealed 5min@210°C	The surface is significantly shinier after annealing and cooling.

Summary of the test results is presented in the table 13.

Table 13. Summary of the test results.

Cooling media	Annealing temperature	Annealing time	**(MEK 2 min), n=30**	**Bending test, n=12**	**Dimensional measurements, n=30**	**Visual inspection n=30**
As molded			NOT OK	75±28 Mpa	-	-
Air	190°C	10 h (BATCH)	OK	38 ±3MPa	no significant changes	no significant changes
	135°C	15 minutes	NOT OK	-	-	-
		30 minutes	NOT OK	-	-	-
	150°C	15 minutes	NOT OK	-	-	-
	190°C	5 minutes	NOT OK	-	-	-
		10 minutes	OK	48±19 MPa	-	-
		15 minutes	OK	-	-	-
		30 minutes	OK	-	-	-
		1 h	OK	39±2 MPa	-	-
	200°C	5 minutes	OK	68±15 Mpa	no significant changes	minor changes
Water		5minutes	OK	69±9 MPa	no significant changes	minor changes
Air	205°C	5 minutes	OK	-	-	-
	210°C	5 minutes	OK	-	significant changes in lenght and diameter	significant change in surface gloss

Based on these test results, the different annealing parameters are evaluated and the conclusions are made on how to precipitate and streamline the annealing method utilized in reducing the residual stresses of the injection molded PPSU fittings

9 DISCUSSION

In this chapter the results of the experimental part of the study are analyzed and compared to previous researches. The reliability of the results is discussed and conclusions of the results are presented.

9.1 Comparison and interfaces with previous research

It can be stated that behavior of PPSU is similar to other amorphous thermoplastics when it comes to residual stresses. The known procedures to optimize the processing parameters in order to reduce the level of residual stresses can be utilized also with PPSU. When the design cannot be changed, melt and mold temperatures play a significant role in reducing the in-mold residual stress level. In order to obtain desired level of residual stresses after annealing, it is important to control the level of residual stresses in as-molded parts.

As stated in the literature, when residual stress level is lowered by annealing, the plastic part becomes more rigid and therefore also less tensile (Cho;Park Seo;Kim;& Lyu, 2012) (Hornberger;Fan;& DeVries, 1986). This was also proven in case of PPSU parts, as the maximum bending stress dropped when the residual stress level was reduced. The effect was the most significant in maximum value of the bending stress (up to -64,9%), but in minimum value the change was smaller (up to -43,3%). The average value of the maximum bending stress decreases quite linearly as the residual stress level decreases. When the standard deviation value is under examination, it can be deduced that the result become more uniform as the residual stress level decreases. The standard deviation of the bending stress for the as molded fitting was 28, when it was only 2 for the fittings annealed for 1 hour at 190°C.

When the result of the dimensional change analysis is studied, it is obvious that when the annealing temperature approaches the T_g, the part suffers from deformation. In the studied case, the parts became oval in shape, the diameter changed in average 0.48% and the length reduces in average 0,52%. In 200°C and less, the dimensional changes are not significant. The most significant change was a small increase in the length (+0,17-0,21%) ,but clear differences between the batch annealing method and the inline annealing simulation could not be detected. The inline annealing shows also only marginal changes to the fittings diameters, as does the batch annealing (<0.1%). In batch annealing the parts are annealed in a big container, but significant dimensional changes cannot be detected, maybe due to low enough annealing temperature (190°C).

The water cooling (quenching) after the annealing was also tested as good results was found with polycarbonate according to Hornberger;Fan;& DeVries (1986). It was discovered, that the quenched samples performed equally in MEK-testing, compared to the samples cooled in air. In these cases, it could be, that the stresses in the part surface have changed in order to provide better chemical resistance, so the stress level cannot be verified. The quenched sample performed better in bending test compared to the air cooled samples. The maximum value and the average were in the same range, but in the minimum value did not decrase as much, when the annealed fitting was quenched.

9.2 Reliability and validity

As the level of residual stresses can vary due to numerous variables in injection molding process and as the MEK-test gives only an indicative result of the level of residual stresses, the results of this study are not unmistakable (Bryce, 1996) (ASTM D7474-17, 2017). Still, the result can be utilized reliably as a base study for the possible inline annealing development project. The reliability of the measurements results is based on the use of calibrated equipment and experienced user of the devices. The reliability of the mechanical testing is based on comparable data from prior internal researches, but as the standard deviation is high (±28MPa) in the results of as molded fittings, the results can be considered as indicative, not precise. These exact test results are not valid for external utilization, because the tests are performed to a specific product, which is not manufactured in any other company.

As there is a limited selection of literature sources concerning the PPSU material, also information provided by the material manufacturer is utilized even though the objectivity can be questionable. Also over 10 years old literature is considered valid in subjects where more recent studies was not found, or in cases where recent studies verify the result of earlier researches. In the field of injection molding, literature from 1980's can still be considered valid, as the basics of the process are still the same.

9.3 Error- and sensitivity analysis

The utilized testing methods are not exact and there is always some variation in the process phases. In order to gain reliable results and improve the repeatability of the result, the tests have been repeated to several samples. In MEK-test, dimensional analysis and visual inspection the number of tested samples was 30, and the results were uniform and in line with the literature review. In mechanical testing the number of tested samples was 12, but still the results are similar to prior internal test results, and the results correlated sensibly with the MEK-test results. The numerical results are mainly presented in the accuracy of the measurement device. The accuracy and resolution of the utilized measurement devices are presented in the table 14. The annealing temperatures are presented in the accuracy of ±2°C due to measured variation caused by the inaccurate temperature adjustment on the utilized infrared oven. The calculated values of the bending stress results are presented in integers, as it was not reasoned to present the result more accurately due to high variation range.

Table 14. Accuracy and resolution of the utilized measurement devices.

	Temperature gauge FLUKE 52 0-230°C	Stopwatch Samsung S7	Scale KERN 0.5-600g	Caliber Sylvac 0-150mm
Accuracy	0.1°C	unknown	0.01g	0.01mm
Resolution	0.1°C	0.01s	0.01g	0.01mm

As all the measurements and test were performed by the same person with the same measurement device, the results are well comparable. When the standard error of mean of the dimensional results is examined, it can be stated, that the error is equal or smaller than the resolution of the measurement device. This refers to good precision, but it does not exclude the possibility for a systematic error. In this research the precision of the measured values is more important than the accuracy of it, as the comparability of the measured values is the base for the conclusions and decisions made, so a systematic error would not have an effect on the decisions made. Due to a reasonable amount of measurement results and simple calculations, the unambiguous mistakes can be effortlessly detected. The summary of the sensitivity analysis is presented in the figure 27.

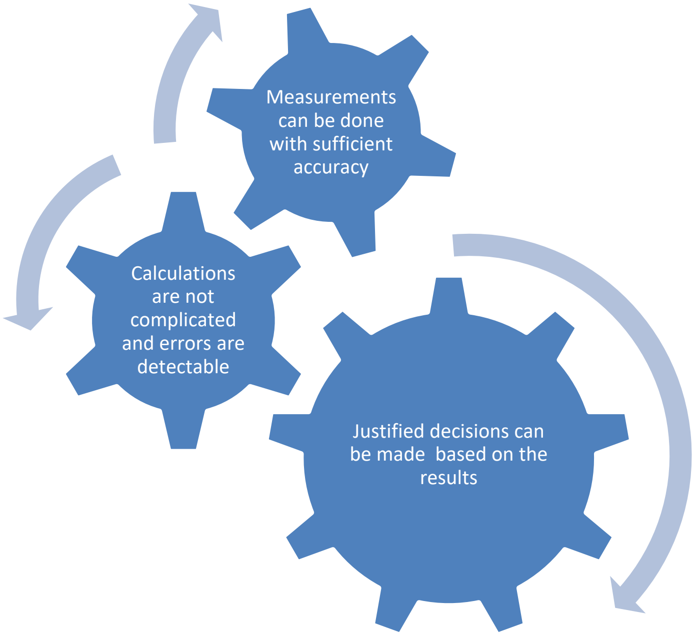


Figure 27. Summary of the sensitivity analysis

9.4 Conclusions

Based on the test results, the residual stress level can be reduced to 4MPa or below in shorter annealing time (5 minutes) when higher temperature (200°C) is set and infrared heating is utilized, but the process could be more error and variation sensitive. The importance of the in-mold residual stress level prior to inline annealing needs to be taken into consideration when the decision to change the annealing method is made. The current batch method most probably allows more variation in the part shape, size and in-mold residual stress level as the inline method as the annealing time is as long as 10 hours. In inline annealing, the annealing time needs to be adjusted to be suitable for each product, and this increases the possibility of human error in the stage of start-ups. This could be solved by adjusting the annealing time according to injection molding cycle time, so that the annealing would last in example 5 injection molding cycles. The thicker/bigger the product, the longer the cycle time, so also the annealing time would automatically be longer for bigger items with thicker wall.

The benefits of the tailored annealing procedures for each item is that the effects on the mechanical properties could be optimized. When the effects of the annealing parameters on the mechanical properties are analyzed, there are clear differences in the results even though the residual stress level is determined to be 4 MPa or less. When the fitting were annealed 5 minutes in 200°C, the average bending stress reduced from 75 MPa to 69 MPa (-8%), and when utilizing the batch annealing method the average bending stress reduced from 75 MPa to 39 MPa (-48%). This could refer, that when shorter annealing time is utilized, the residual stress level is still near 4 MPa, but after batch annealing the residual stress level approaches 0 MPa. This should be studied further in order to determine is the 4MPa residual stress level adequate in order to fulfill the requirements set for the PPSU fittings, or should the residual stress level be closer to 0 MPa, even though the effects on the mechanical properties are more significant.

In the literature review it was stated, that the residual stresses can be reduced just by adjusting process parameters. So, why do we need annealing? The problem is, that even though the residual stress level could be minimized, the products have a lot of other quality properties, such as visual appearance, mechanical endurance and dimensions. If the process is optimized just by looking at the residual stress level, the other properties would be compromised. In injection molding the process parameters are usually a compromise in order to achieve the best possible outcome. In some cases the as-molded residual stress level might be even higher than 10 MPa due to these compromises. In these cases the possible inline annealing processes parameters should be re-evaluated. And if the product and mold design has significant effect on the residual stress level, then why do not we make such a design, that there will be no stresses? Yes, another compromise; it would probably be quite difficult to connect pipelines with a thin sheets of plastics instead of easily installable, durable, flow-optimized and leakage proof fitting. Still, with optimal structural design of the mold cooling channels, and with right choices in mold and core materials the residual stress level can be affected without compromises in the product design.

As end conclusion it can be stated that annealing is a necessary after treatment for PPSU fitting for applications where chemical resistance properties are demanded and a compromise has to be made in expense of mechanical properties. The annealing time can be diminished if the annealing is done utilizing an inline method, where the parts are heated to maximum of 200°C temperature for minimum of 5 minutes time without cooling to room temperature after molding and the material mass is reasonable. The effect on the mechanical properties and part dimensions is reduced if the annealing process is optimized. It was verified that this can be performed with reasonable costs utilizing simple conveyor belt infrared oven and acquiring expensive high-tech equipment is not necessary.

9.5 Novelty value of results

Even though plenty of prior researches is done from residual stresses and injection molding, in example Adhikari;Bourgade;& Asundi (2016) and Guevara-Morales & Figueroa-López (2014), in none of them annealing of PPSU was studied, so as a result of this research, new knowledge has been formed.

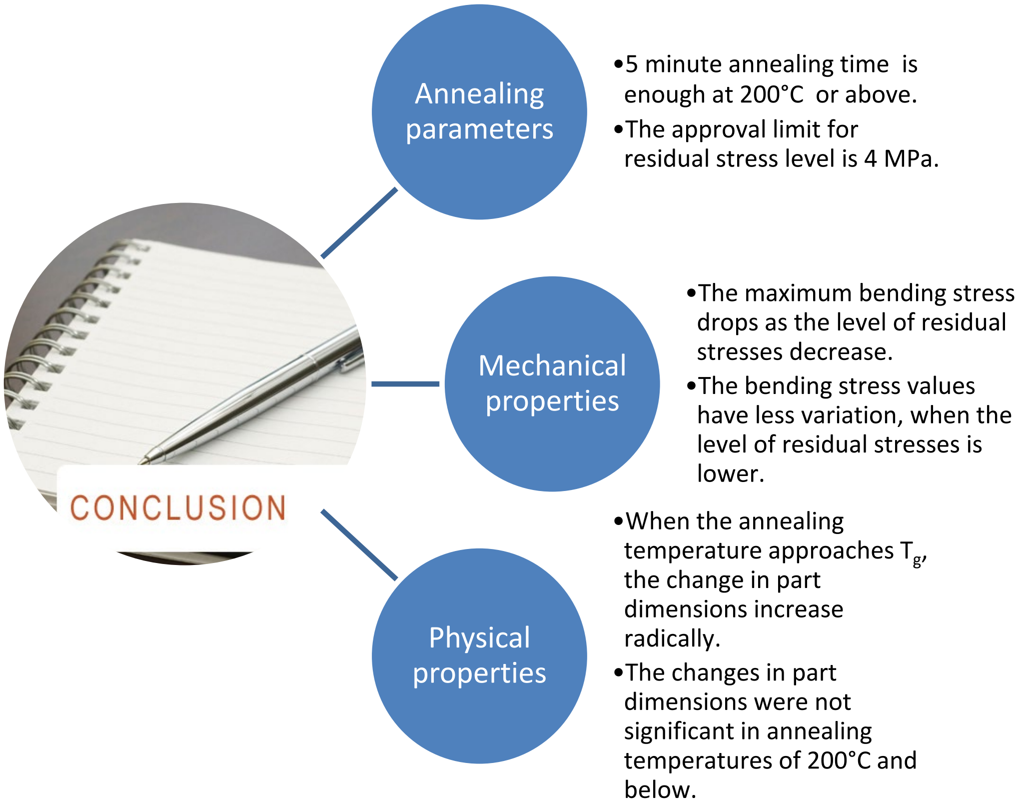
9.6 Generalization and utilization of results

This research verifies, that the basic properties and behavior of amorphous thermoplastics can be applied to PPSU as prior researches of this subject was not found in literature review. The results of this study can therefore utilize in similar studies of other amorphous thermoplastics in some extend.

9.7 Topics of future research

In this field of science a lot is still unstudied. More profound study of residual stress development in PPSU parts and the effect of the injection molding parameters to them is an excellent topic to study more of. When it comes to annealing procedure and equipment, hardly any studies has been made, or at least are available, so there is plenty of room for further studies in that field. Can the infrared or hot air oven be replaced with another form of radiation? Is air the best media for annealing, or can some other gas or liquid be utilized without safety risks? Does the thermal conductivity of the plastic material have an effect on the level of residual stresses? A research arises even more questions as it answers, I presume.

The test results showed that the annealing temperature in inline annealing has to be more than 190°C if the annealing time has to be less than 10 minutes in order to reduce the residual stress level to 4MPa or below. The bending test result showed that when PPSU fitting are annealed, they become more rigid, but also the mechanical properties become more stable. Dimensional changes increase significantly in 210°C annealing, as the temperature approaches the Tg. Also changes in visual appearance increase in higher annealing temperatures. The main conclusions are presented in the figure 28.



- 5 minute annealing time is enough at 200°C or above.
- The approval limit for residual stress level is 4 MPa.

- The maximum bending stress drops as the level of residual stresses decrease.
- The bending stress values have less variation, when the level of residual stresses is lower.

- When the annealing temperature approaches T_g, the change in part dimensions increase radically.
- The changes in part dimensions were not significant in annealing temperatures of 200°C and below.

Figure 28. The main conclusions of the research.

10 SUMMARY

The goal of this research was to reconcile how to precipitate and streamline the annealing method utilized in reducing the residual stresses of the injection molded PPSU fittings. The efficiency of the current method was verified by determining the level of residual stresses after the annealing utilizing MEK-test, which was a simplified chemical testing method of the ASTM D7474-17 and the Solvay method, mechanical properties were determined with bending test and the physical properties were studied via dimensional measurements and visual analysis. The tests results verified that the residual stress level is efficiently reduced when the batch method is utilized, but the negative effect to mechanical properties was apparent. No significant dimensional changes could be detected. The efficiency of reducing the residual stress level is based on long annealing time, which is not efficient on ecological or economical point of view. By defining the parameters for possible inline annealing method, it was proven that it is possible to reduce the level of residual stresses to the required 4 MPa level in significantly shorter time. It was also detected, that by fine tuning the annealing parameters, the effects on mechanical properties and dimensional changes can be diminished.

The research problem in the material technological point of view was defining and reconciling of the product properties, annealing parameters, polymer properties, manufacturing process parameters, fitting geometry and annealing circumstances. In theoretical section of this study the formation mechanism of residual stresses was studied in order to understand how the level of residual stresses can be adjusted and controlled in the injection molding process of PPSU fittings. The requirements for plastic fitting were determined in chemical, mechanical and physical point of view. The possible scale for annealing parameters was determined based on material manufacturers guidelines and material properties, such as T_g and the mold temperature. The first research question was: How does the residual stress level of the products change in the annealing process and why? To answer this question, an answer for another question was required: What is the formation mechanism of the residual stresses in injection molding? In literature review it was stated that the polymer chain relaxation and the restrictions of this relaxation appears to be the reason for the formation of residual stresses in injection molding process. It was also stated that annealing is performed in order to allow the molecular chains to relax. This means that the utilized annealing temperature should be near the T_g of the polymer material. In experimental part of this research different annealing temperatures and times were tested. It was noticed that in higher temperatures the residual stress level is reduced faster, so it can be deduced that the relaxation of the polymer chains is faster in higher temperatures. It was also noticed that when the annealing temperature approached the T_g, the polymer chains began to move and so dimensional changes could also be detected in the fittings.

The second research question was: What options are available for replacing the current annealing method? This question was followed by a sub question: Is a continuous type of annealing process as efficient in releasing internal stresses as the current batch annealing method as the annealing time needs to be significantly shorter? Options for replacing the current batch annealing method was sought via literature review, but a lack of reliable literature sources was discovered. The possible option was found in conveyor belt -type of infrared oven annealing, which was simulated utilizing a laboratory size infrared oven in the experimental part of the study. The continuous type of annealing method was discovered to reduce the residual stress level to the required level of 4 MPa in 5 minutes, when the annealing temperature was 200°C, but it was concluded that in the batch annealing method the level of residual stresses are reduced possibly near 0 MPa. In the bending test none of the fittings annealed for less than 10 minutes gave similar results as the batch annealed fittings. So it can be stated that a continuous type of annealing is not as efficient in releasing residual stresses as the batch annealing method, but it is efficient enough when the required level of residual stresses is 4 MPa or less.

The third research question was: What parameters/ annealing time is sufficient for gaining adequate relaxation of residual stresses and with what methods this should be assured? And a sub question followed: Is it possible to precipitate the annealing process by rising the processing temperature and what effects does the temperature have on the properties of the products? The sufficient annealing temperature was 200°C, as 5 minutes annealing time was enough to gain the required level of residual stresses (4 MPa or less). In 190°C the required annealing time would be 10 minutes in order to reach the required residual stress level. As a specific limit for the level of residual stress has been set by the target company and the material manufacturer (4

MPa), the 2 minute MEK-test based on the ASTM D7474-17 -method and the Solvay -method was utilized as it was the most suitable for this research compared to other possible methods, such as hole drilling method or birefringence measurement. It was discovered that it is possible to precipitate the annealing process by rising the annealing temperature. If the annealing temperature approached T_g, the dimensions of the fittings changed significantly compared to annealing in lower temperatures.

The fourth research question was: What effects has the annealing parameters have on the chemical, physical and mechanical properties of the PPSU fittings? The effects on the chemical properties was studied in the literature research and tested utilizing the 2 minutes MEK-test. It was discovered that the more the residual stress level is reduced in the annealing process, the more resistant the PPSU fitting is against Methyl Ethyl Ketone. Also based on the literature review and the ASTM D7474-17 –method, the resistant against many other chemicals is also increased due to the reduction in the level of residual stresses. In the physical properties no significant changes was detected until in the annealing temperature of 210°C, as the annealing temperature approached the T_g. The effects on the mechanical properties were quite clear. The more efficient the annealing procedure was in reducing the level of residual stresses, the more effect on the bending stress could be detected.

In this research, the following hypothesis were presented:

1. The residual stress level of the PPSU fittings can be decreased in shorter annealing time, if the annealing temperature is increased from the currently utilized level.
2. Increasing the annealing temperature near to glass transition temperature (T_g) can cause unwanted dimensional changes to the PPSU fittings.
3. The changes in mechanical properties of the PPSU fittings can be controlled more precisely in inline annealing compared to the batch annealing.
4. Batch annealing is more forgiving to the changes in the residual stress level of the as molded PPSU fittings compared to the inline annealing.

The first two hypothesis could be verified in the experimental part of this study. In the mechanical testing it was noticed that minor adjustments can have radical impact on the bending stress. Based on this knowledge it can be deduced that it would be possible to control the effect of annealing on the mechanical properties of the PPSU fitting more precisely, if inline annealing- method and tailored parameters per product is utilized, so this would verify also the third hypothesis. The fourth hypothesis cannot be verified based on this research, before more experience of the inline annealing is gained. Still, if inline annealing is utilized, the annealing parameters need to be verified separately to each product, as in batch annealing same parameters are utilized to all products.

It can be summarized that the main goals of this study were reached and the research questions were answered in some extend. The hypothesis presented were mainly verified. Based on the knowledge collected and produced in this study, the inline annealing method can be considered as an option for the batch annealing method, but before development project could be initiated for acquiring and implementing the inline annealing equipment, the costs and benefits of the investment are to be evaluated.

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