

Kinetic of Curing at the Interface Rubber-Rubber

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2. Koncepce metodiky měření pro analýzu kinetiky vulkanizace pryž-pryž dílů.
3. Stanovení teoretického základu pro metodiku měření.
4. Návrh geometrie zkušebního vzorku.
5. Návrh upínací svorky zkušebního vzorku pro současné testovací zařízení.
6. Příprava kaučukových směsí.
7. Charakteristika reologických vlastností.
8. Provedení analýzy vulkanizace na rozhraní pryž-pryž dílů.
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[2] R. N. Datta, Rubber Curing Systems (Rapra Review Reports), Vol. 12, 2002, ISBN-13: 978-1859573266

[3] James Lindsay White, Rubber Processing: Technology, Materials, and Principles, Hanser Gardner Publications, 1995, ISBN-13: 978-1569901656

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ABSTRAKT

Tato diplomová práce se skládá ze dvou částí a je zaměřena na popis kinetiky vulkanizace na rozhraní dvou pryžových komponentů. Teoretická část je zaměřena na charakteristiku kaučukové směsi a také na popis kinetiky vulkanizace a parametrů, které ji ovlivňují. Nakonec je stručně vysvětlena kinetika vulkanizace na rozhraní pryž-kov, která zahrnuje důležité poznatky pro koncepci metodiky měření.

V experimentální části je uveden postup návrhu zkušebního tělíska, formy pro lisování a upínacího zařízení a také stručný popis měřícího zařízení. V další části je zahrnuta příprava kaučukových směsí a stanovení jejich reologických vlastností. Měření je prováděno při dynamickém namáhání na dynamickém mechanickém analyzátoru (DMA), kde je detekována adhezní síla v závislosti na čase. Výstupem celé práce je vulkanizační křivka.

Klíčová slova: kinetika vulkanizace, rozhraní, kaučuková směs, DMA, adhezní síla, pryžové komponenty

ABSTRACT

The presented master's thesis is divided into two parts and is devoted to the description of curing kinetics at the interface of two rubber components. The theoretical part deals with rubber compound characterization and also with description of curing kinetics and parameters affecting it. What is more, curing kinetics between rubber-metal components, which includes important findings for the concept of measurement methodology, is also briefly explained.

Design of a testing sample, pressing mold and holding clamp as well as the measuring equipment are described in the experimental part. It also deals with the preparation of rubber compounds and determination of their rheological properties. The measurement is performed at dynamic loading by dynamic mechanical analyzer, where the dependence of the adhesion force and time is detected with the curing curve as an output.

Keywords: kinetics of curing, interface, rubber compound, DMA, adhesion force, rubber components

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I hereby declare that the printed version of the Master's thesis and its electronic version deposited in the IS/STAG system are identical.

In Zlín 19. 5. 2017

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Michal Drobilík

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INTRODUCTION

Curing is a process whereby chemical crosslinks are created between the chains of rubber molecules, resulting in the formation of a three-dimensional network. The reaction proceeds under elevated temperature and pressure to form elastic material. As this reaction is extremely complex, it is difficult to describe its course.

Currently, there are several methods to monitor the process and to analyze the product. Mooney viscometer, oscillating disc rheometer (ODR), moving disc rheometer (MDR), calorimetry techniques or rubber process analyzer (RPA) are applied in measurement. Determined parameters include the cure enthalpy, reaction rate and activation energy.

This work is focused on rubber parts in the automotive industry, highly dynamically loaded components commonly composed from varied rubber sheets. Mechanical behavior of such rubber parts is based on dynamic loading conditions due to complex processes. The most affected region in such a more-layer component is the interface connection between rubber-rubber transferring the high dynamic loading condition applied on the loaded part.

Presently, experimental methodology describing curing kinetics between two rubber layers to understand and describe the complete kinetics process has been rarely known. Therefore, the aim of this thesis is to develop an experimental methodology to evaluate rubber-rubber curing kinetics for automotive application. This technique should be easily feasible, inexpensive and innovative in the rubber industry. (1; 2)

I. THEORETICAL PART

1 CURING

Basic raw material for curing is rubber, which is soft, sticky thermoplastic material with poor mechanical properties. Therefore, rubbers were not suitable for usage in the industry for a long time. The first mention about rubber curing was recorded in 1839 by Charles Goodyear, who discovered curing by sulfur to obtain improved properties of rubber.

As mentioned above, curing is a transformation of rubber from plastic into elastic material due to the three – dimensional network of rubber chains. The reaction proceeds under elevated temperature and pressure. (3)

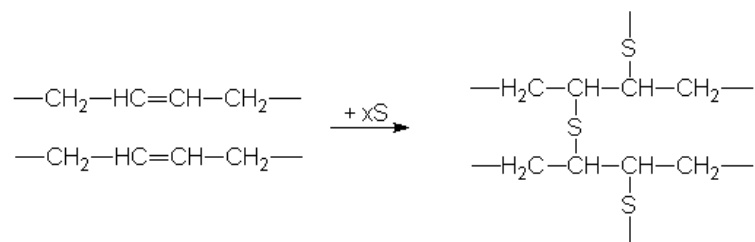


Figure 1 – Principle of curing by sulfur (4)

1.1 The course of curing

The course of curing may be measured by Mooney viscometer, which transmits an oscillating torsional strain to a sample under pressure at elevated temperature. As a result is curve of curing, which is expressed as dependence of torque on time. This chapter describes attributes of the curve. Curing kinetics is explained in Chapter 2.

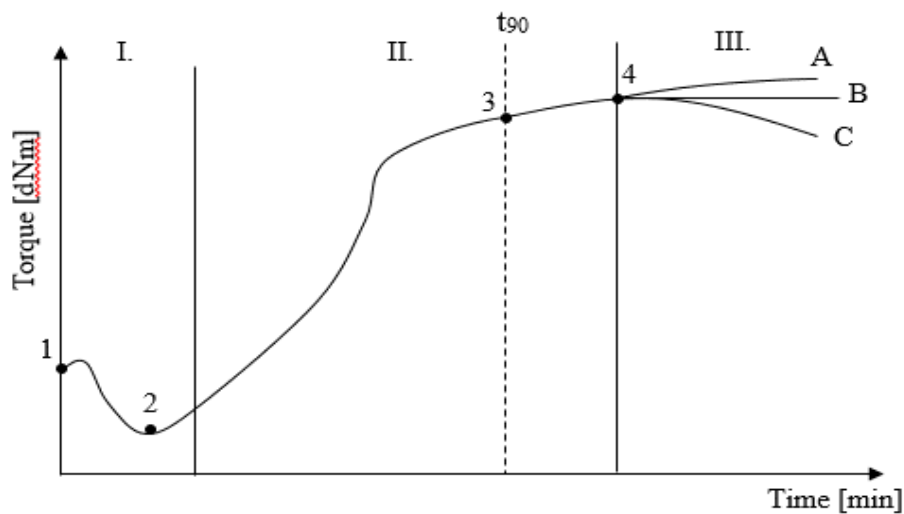


Figure 2 – Curve of curing

Curve of curing has these sections:

Section I. – This section is also called as an induction period or safety of rubber compound. It is a period when the compound is gradually heated, thereby viscosity of compound decreases. Crosslinking reaction does not take place yet. Only the reaction of a vulcanization agent with rubber and other ingredients occurs. Rubber compound could be manipulated safely.

Section II. – Three-dimensional network due to rubber chains bonding is formed in this section. The amount of vulcanization agent gradually decreases and the strength of network gradually rises. Point 3 in the graph expresses the optimum of vulcanization with 90 % of conversion.

Section III. – Point 4 depicts 100 % of conversion. However, curing reaction may continue in three different ways affecting the network structure.

Curve A – If the vulcanization agent is not completely utilized, the curve of curing shows an upward trend, network density increases and quality of vulcanizate properties decreases. Vulcanization agents performing such effect include zinc oxide or manganese oxide.

Curve B – The vulcanization agent has been completely used for the reaction. The course of curing curve and properties of vulcanizate have remained unchanged. Vulcanization agents causing such behavior are organic peroxides.

Curve C – This effect is called a reversion and is typical for natural rubber vulcanized by sulfur. Density, network structure, module decrease and vulcanizate degrades during the reversion. (5; 6)

1.2 Rubber compound

Rubber compound contains a lot of additives added to improve workability and final compound properties. The composition of compound depends mainly on price and customer's requirements. The ratio of rubber and other additives determining workability and resulting compound properties is very important.

1.2.1 Composition of compound

Compound composition is based on raw rubber, filler, antidegradant, antioxidant, curing system and other additives and the precise composing depends on the required properties.

Rubber compound is commonly based on raw rubber or on a blend of a variety of raw rubbers. Other additives are expressed in parts per hundred rubber or phr. The total of the parts for one or more different rubbers in the compounding is always 100. All other additives are in the ratio against 100 parts of rubber. (7)

Table 1 – Sample rubber recipe (7)

| Ingredients | Parts per hundred rubber (phr) |
|--------------------------|---------------------------------------|
| Rubber | 100 |
| Filler | 50 |
| Antidegradant | 1,5 |
| Activator | 4 |
| Accelerator | 2,5 |
| Vulcanizing agent | 1,7 |

1.3 Rubber

Rubbers or elastomers belongs to the amorphous polymers group. These materials are main and the most important part of the rubber compound. In this thesis four types of rubber, which are described in following chapters, are used.

Their most important property is the ability to undergo large elastic deformations which means they stretch and return to their original shape. Rubbers are elastic at low temperatures and plastic at high temperatures. Furthermore, they are also soft, flexible and resistant to abrasion. These mentioned properties may be improved by additives and curing prepared compound. (8)

1.3.1 Natural Rubber (NR)

Natural rubber is derived from the latex of the rubber tree (*Hevea brasiliensis*). This tree is grown mainly on plantations in Asia. The amount of dirt in natural rubber determines the cost of rubber in the marketplace.

Natural rubber is obtained by coagulation in the presence of acid. Small quantities of anti-branching agents are added to the latex before the coagulation in order to keep the viscosity of natural rubber.

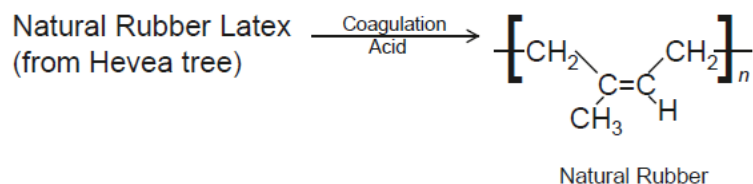


Figure 3 – Derivation of natural rubber (9)

Natural rubber has a wide range of applications as its structure contains long chains providing good mechanical properties of products. It is mainly used as a blend with SBR or BR for the tire production as well as for various automotive components, such as vibration isolators, dampers or motor mounts. (8)

1.3.2 Butadiene Rubber (BR)

BR is the third mostly used rubber in the rubber industry. The main area of its consumption is the tire sector. BR performs unique properties, such as excellent wear resistance, flex fatigue resistance and dynamic properties.

Butadiene rubber is a homopolymer made from butadiene monomer. This rubber may be prepared by solution or emulsion polymerization. (9)

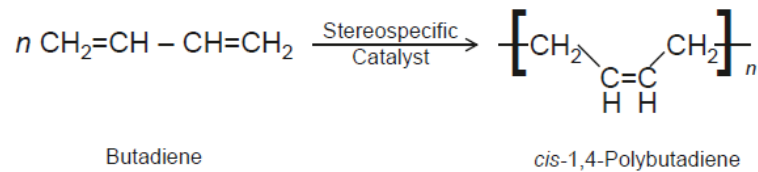


Figure 4 – Production of cis-1, 4-polybutadiene (9)

1.3.3 Styrene Butadiene Rubber (SBR)

SBR is the mostly used synthetic rubber in the rubber industry. Its production is cheap, which may explain its wide application, especially in the tire production. It is also employed in the manufacture of conveyor belts or industrial hoses.

SBR is a copolymer prepared from styrene and butadiene monomers. This copolymer may be prepared by three different methods. The first is a hot emulsion polymerization in aqueous soap emulsion at the temperature of 50 °C. The next one is a cold emulsion polymerization in aqueous soap emulsion at the temperature of only 5 °C. The last method is a solution polymerization in anhydrous organic solvent. (8)

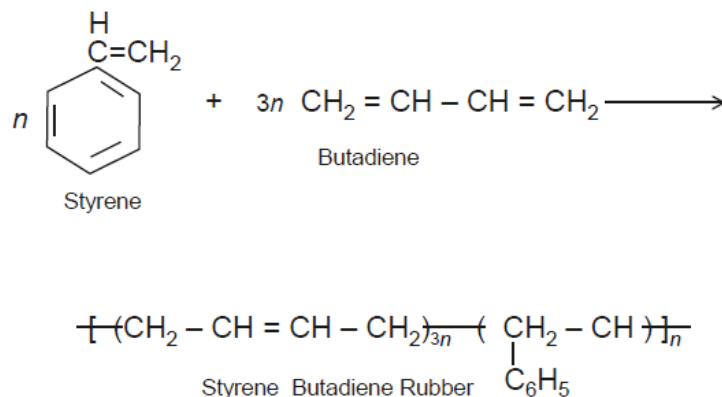


Figure 5 – SBR polymerization process (9)

1.3.4 Ethylene Propylene Diene Rubber (EPDM)

EPDM is the fourth mostly applied elastomer in the rubber industry, especially in tire sidewall compounds, cover strips and bicycle tires. It is also commonly used in roofing and automotive weather-strips.

Beneficial properties of EPDM are good aging resistance, resistance at higher temperatures, resistant to oxygen, ozone and sunlight attack.

EPDM is a terpolymer produced from ethylene, propylene and diene monomer. The reaction proceeds in the presence of Ziegler-Natta catalysts providing advantageous properties of EPDM. (8; 9)

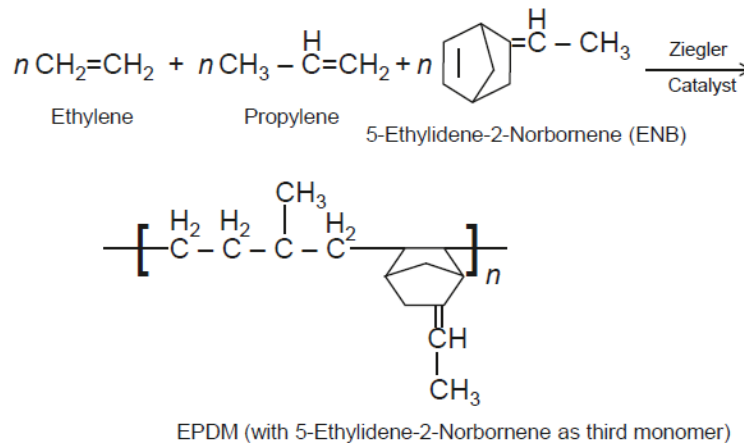


Figure 6 – Example of production of EPDM (9)

1.4 Fillers

Fillers are particulate materials, which may vary in size and shape. Generally, they are used to improve rubber compound properties, such as tensile strength, stiffness, adhesion or wear resistance. Further function of fillers is to reduce the cost of rubber compound.

Fillers are divided according to effect on the compound properties into three categories:

- a) **Reinforcing fillers:** These additives increase tensile strength, structural strength and abrasion resistance. The particle size varies from 0.01 to 0.1 μm . This group of additives includes fine carbon black or precipitated silica.

- b) Semi-reinforcing fillers:** This group of additives shows similar properties as the previous one, but abrasion resistance is not enhanced. The particle size is from 0.1 to 1 μ m. Coarse carbon black, hard kaolin and precipitated CaCO₃ are included in this group.
- c) Non-reinforcing fillers:** These additives perform no effect on properties of rubber compound, but their main function is to reduce the cost of rubber compound. The particle size is from 1 to 10 μ m. Talc and CaCO₃ belong to this group. (10)

1.4.1 Carbon black

Carbon black is the most important filler in the rubber industry as it significantly enhances cured rubber properties, such as ultimate tensile strength, hardness, wear resistance and tear resistance. Classification of carbon black is divided according to a particle size and production method. (11)

Table 2 – Carbon black classification (7; 8; 9)

| Grades | Description | Identification | Particle size [nm] |
|--------------------|-------------------------------------|----------------|--------------------|
| N100 - N199 | Super abrasion furnace | SAF | 11 to 19 |
| N200 - N299 | Intermediate super abrasion furnace | ISAF | 20 to 25 |
| N300 - N399 | High abrasion furnace | HAF | 26 to 30 |
| N400 - N499 | Fast furnace | FF | 31 to 39 |
| N500 - N599 | Fast extruding furnace | FEF | 40 to 48 |
| N600 - N699 | General purpose furnace | GPF | 49 to 60 |
| N700 - N799 | Semi-reinforcing furnace | SRF | 61 to 100 |

Furnace carbon black is the most widely used. Its production is performed through an incomplete combustion of a spray of liquid oil feedstock into a mixture of natural gas and preheated air in a refractory furnace. The processing temperature is from 1200 to 1600 °C.

(11)

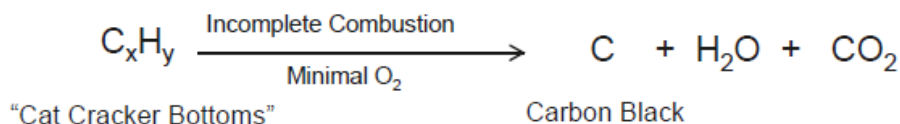


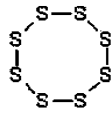
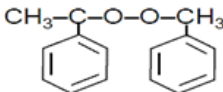
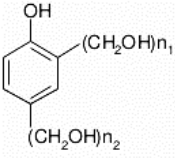
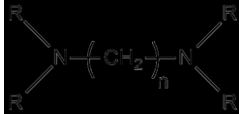
Figure 7 – Production of furnace carbon black (9)

1.5 Vulcanizing agents

These substances are capable of creating bonds by chemical reaction between the macromolecules of elastomer. Particular vulcanizing agent must be used only for the specific type of elastomer as each agent gives specific properties to vulcanizate.

Sulfur is used as a vulcanizing agent for about 90 % of all rubber compounds. For curing by sulfur is necessary that elastomers contains some chemical unsaturation, such as carbon-carbon double bonds. Remaining 10 % of rubber compounds employ curing systems based on peroxide curatives. Furthermore, there exist rubber compounds based on halogenated elastomers, which need metal oxides for curing, and also resin cures used in specific cases, such as bladders for tires. In this work, sulfur has been used as a vulcanizing agent to prepare rubber compounds. (8; 9)

Table 3 – Curing agents, their chemical composition and example of use (9; 12; 13)

| Curing agent | Chemical composition | Example of elastomer |
|---|---|----------------------|
| Sulfur (S₈) |  | NR, BR, SBR, EPDM |
| Peroxides (Dicumyl peroxide) |  | EPDM |
| Resin (Phenol-formaldehyde) |  | EPDM, IIR |
| Diamines |  | FKM |
| Metal oxides (Zinc oxide) | Zn – O | CR, IIR |

1.5.1 Sulfur

Sulfur is now the most common vulcanizing agent used in the rubber industry. Sulfur reacts with chains of rubber and creates crosslinks between them. Various kinds of sulfur differs according to a particle size and content of oil improving workability of compound. The amount of sulfur also determines the hardness of rubber.

Sulfur is a byproduct of the natural gas industry. Perhaps 80 to 90 % of sulfur needed for the rubber industry is recovered from natural gas or petroleum. (8)

1.6 Activators

Zinc oxide and stearic acid are two most common activators used with sulfur cure systems. These ingredients added to late in the mixing cycle and react until the rubber compound is heated to curing temperature. Typically, activators are applied at small concentrations from 0.2 to 5 parts per hundred parts of rubber.

Stearin acid reacts with zinc oxide during the curing process to solubilize divalent zinc ion. Then, zinc ion reacts with organic accelerator and thus enables eight-membered ring of sulfur molecule to break and establish sulfur crosslinks between rubber molecular chains. (9)

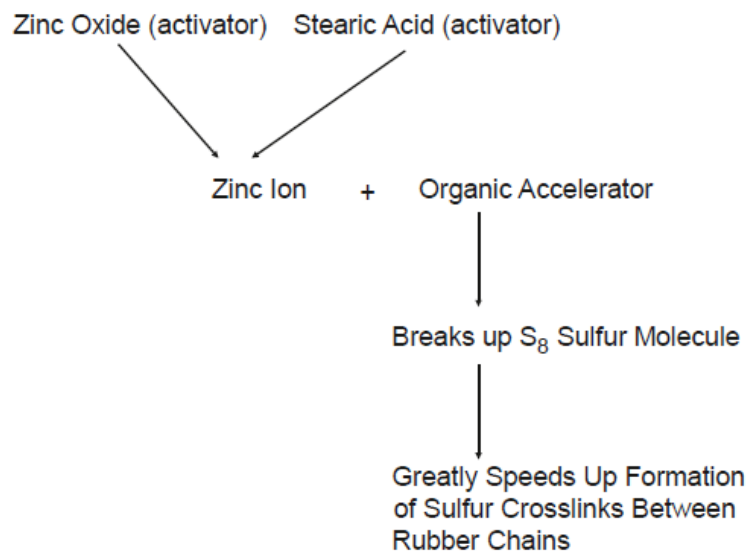


Figure 8 – Sulfur activation for curing of rubber (9)

1.7 Accelerators

Accelerators may be commonly used in rubber compound to impart a cure rate and state of cure. A lot of diverse types of accelerators could be used in the rubber industry.

In this work CBS (N-cyclohexyl-2-benzothiazolesulfenamide) accelerator has been used. It imparts a significant level of scorch safety to compound, relatively fast cure rate and high crosslink density. CBS is classified as sulfenamide accelerator, which is similar to TBBS (N-tert-Butyl-2-benzothiazolesulfenamide). (8)

1.8 Antidegradants

Antidegradant is a substance that is added to retard deterioration of vulcanized rubber compound. Deterioration could be a result of chemical attack causing a loss of functional properties and decrease in a service lifetime of rubber product. According to the agent attacking rubber protective substance is selected. (8)

IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine), which belongs to a group of antioxidants, has been applied in this work. IPPD is a high activity antioxidant used primarily for ozone resistance and it provides a compound protection against catalytic degradation by copper and other heavy metals. (14)

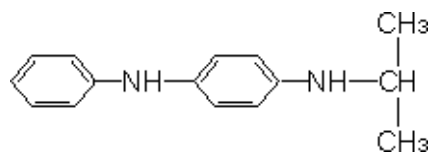


Figure 9 – Structural formula of IPPD (14)

2 CURING KINETICS

Kinetics is a technique that is used to describe individual sections of vulcanization and facilitates a proposal of processing and vulcanization of rubber. Parameters necessary for processing are obtained from description of kinetics. Curing mechanism and vulcanization kinetics parameters contribute to a correct choice of curing temperature and time.

2.1 Kinetics parameters of curing

Vulcanization is a chemical reaction, which could be described by chemical equilibrium and chemical kinetics. (15)

a) Scorch safety (t_2)

Scorch safety refers to the time when the compound remains plastic. This time marks the point at which the plastic material begins the chemical conversion to elastic network with torque increased by 2 dNm above the minimum. Each type of rubber has its specific scorch safety depending on the rubber composition.

b) Rate of cure (R)

Cure rate describes the rate at which crosslinks are formed. After the point of scorch, chemical crosslinking continues providing more crosslinks. The cure rate determines how long a compound must be cured in order to achieve optimal properties.

c) Cure time (t_{90})

Cure time is the time needed to achieve a desired state of cure. In practice, time t_{90} required to reach 90 % of the maximal cure is used.

d) State of cure

State of cure is expressed as a percentage of maximal attainable cure and describes a degree of the compound crosslinking (15)

2.1.1 Calculation of module at time

This calculation is an indirect method to evaluate curing. Module is measured at different times, but in practice module is evaluated at time t_{90} using the following formula: (16)

$$M_{90} = M_M + 0.9 \cdot (M_H - M_M) \quad [1]$$

Where:

M_H – Maximal torque [dNm]

M_M – Minimal torque [dNm]

This formula can be modified to calculate the degree of crosslinking: (17)

$$\theta = \frac{M_t - M_M}{M_H - M_M} \quad [2]$$

Where:

M_t – Torque at curing time t [dNm]

2.1.2 Dependence of concentration on cure rate

Curing of rubber is a rather complicated chemical reaction, which consists of a lot of simple reactions between the components of compound. In practice it is important how long the curing takes and how it changes the concentration of curatives. Cure rate is generally expressed according to the formula: (6)

$$R = \frac{dc}{dt} = -K \cdot c^n \quad [3]$$

Where:

c – Initial concentration [-]

t – Time [s]

K – Rate constant [s^{-1}]

n – Reaction order [-]

2.1.3 Dependence of cure rate on temperature

Temperature greatly affects the cure rate as rubber compound must be heated to initiate the curing. This dependence is expressed by Vant Hoff reaction isochores: (6)

$$\frac{dk}{dT} = \frac{E \cdot k}{R \cdot T^2} \quad [4]$$

By adjusting this formula Arrhenius equation is obtained:

$$k = A \cdot e^{\frac{-E}{\Delta T \cdot R}} \quad [5]$$

Where:

k, A – Rate constants [s^{-1}]

E – Activation energy [$J \cdot mol^{-1}$]

$e^{\frac{-E}{RT}}$ – Boltzmann factor [-]

2.2 The mechanism of sulfur curing of rubber

Initiation: This step involves a decomposition of portion of sulfenamide or sulfenimide accelerator and reductive cleavage –S–N– bonds by using sulfur. The initiation reaction liberates a quantity of amine, which then may react with S_8 to generate activated sulfur essential for other reactions.

Induction: In this step sulfur reacts with accelerator disulfides, sulfenimides and sulfenamides. As a result, accelerator polysulfides and disulfides form.

Activation: Accelerator polysulfides and disulfides are depleted to create MBTS_x, present as zinc complexes. Sulfenamide accelerator is completely utilized at the end of this step.

Sulfurization and crosslinking: After all sulfenamide, di- and polysulfides are utilized, polymer is sulfurated and crosslinked simultaneously. (1)

2.3 Effect of different parameters on course of curing

The course of a vulcanization curve is dependent on the content and properties of individual components of compound and also on processing conditions. The following chapters describe the influence of various parameters, such as the type of additive, temperature or composition of compound on the course of curing.

a) Effect of activator on cure rate for natural rubber

Activators are either organic or inorganic and they perform a significant influence on the course of curing.

As shown in Figure 10, zinc oxide has a profound effect on the extent of cure in accelerated sulfur vulcanization. To improve the rate and efficiency of sulfur vulcanization it is important to use the combination of zinc oxide and stearic acid. Conversely in the absence of an accelerator (TBBS), zinc oxide and stearic acid are rather ineffective in increasing crosslinks production. (15)

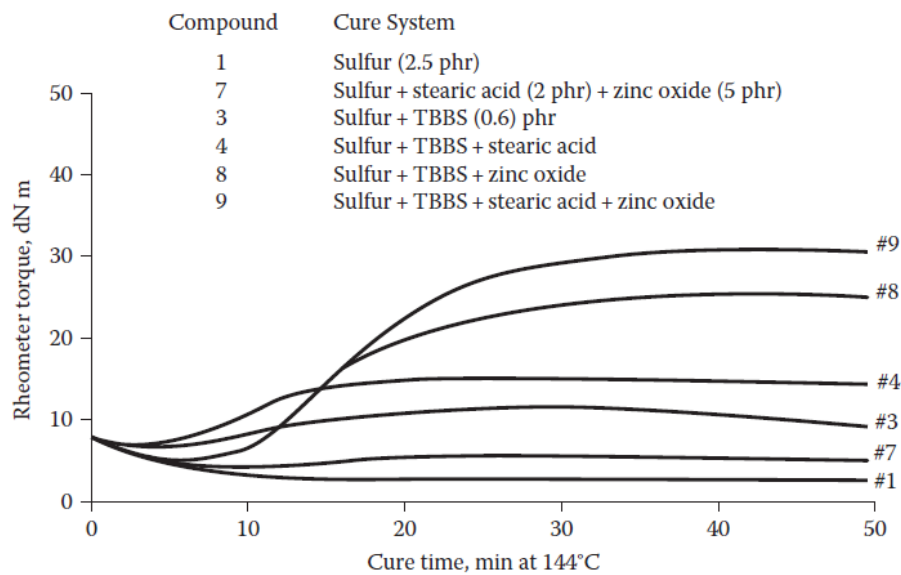


Figure 10 – Effect of activators on cure rate for natural rubber (15)

b) Effect of temperature on cure kinetics for different rubber compounds

Rubber compounds based on natural rubber and styrene-butadiene rubber were prepared by solution mixing and vulcanized by sulfur at 433 K and 443 K.

According to published studies, NR/SBR blends are immiscible and exist in two phases. As shown in Figure 11, reactivity of NR is higher if compared with SBR. Pure samples of NR reach maximum torque for time lower than pure SBR samples. For time $t > t_{100}$, NR pure compound shows a reverse behavior. In all NR/SBR blends NR phases appear over-cured. (18)

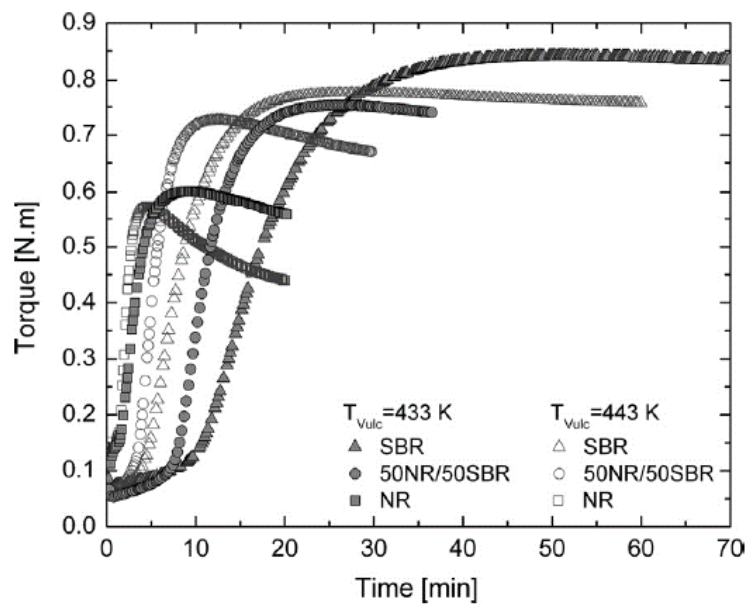


Figure 11 – Dependence of torque on time for prepared samples (18)

c) Effect of type accelerator on curing of SBR

The response of elastomer to a specific accelerator varies with the number and activity of present double bonds. Natural rubber and styrene butadiene rubber contain a lot of double bonds.

As shown in Figure 12, the fastest course of curing is reached with CBS and TBBS accelerators application. The Scorch delay is longest for MBS and shortest for MBTS.

Thiazoles (MBS, MBTS) perform slower cure rate, shorter processing safety and lower modulus than sulfenamides (CBS, TBBS) do. (15)

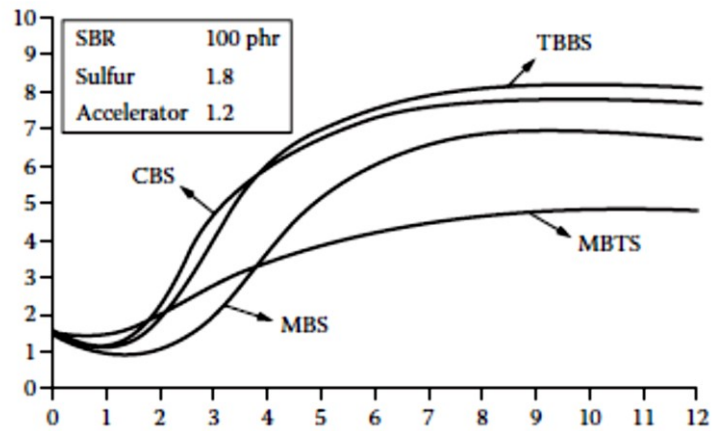


Figure 12 – Effect of type accelerator on course of curing at 160 °C (15)

d) Effect of different carbon black on curing of EPDM

Five types of carbon black were used for the measurement and curing kinetics was determined by rheometer at 160 °C for 20 minutes. Information, such as the composition of compounds, is listed in the article. (19)

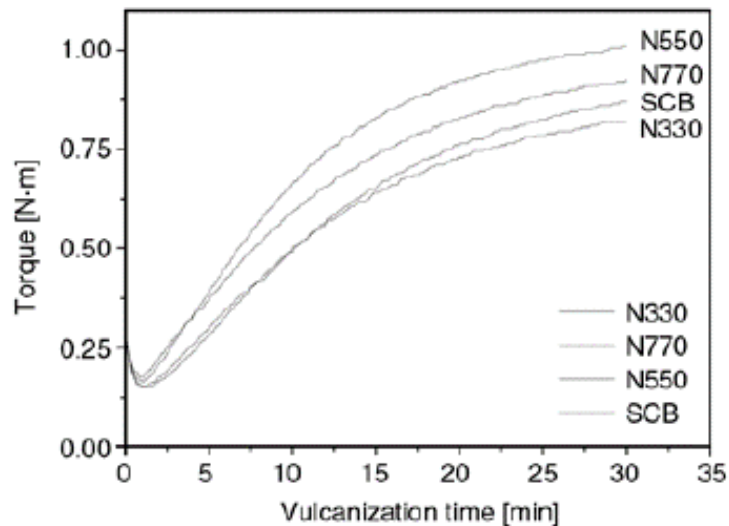


Figure 13 – Curing curves of EPDM/carbon black composites (19)

The course of curing for individual compounds is dependent on the properties of carbon blacks, such as a particle size, size of specific surface and content of chemical elements. (19)

2.4 Curing between rubber-rubber

Curing between rubber-rubber components has not been described in detail yet. However, a mechanism rubber to metal exists and provides valuable findings for the concept of measurement methodology. Currently, blends of rubbers are used for various applications, but it is not the same as curing of separate specific rubber components.

Description of kinetics between rubber-rubber components is the aim of this master thesis. Measurement results and description of kinetics will be listed in the experimental part of this work.

2.5 Bonding between rubber-metal

Rubber to metal bonded assemblies are used in a wide range of industrial applications, such as to reduce vibrations or noise, but this process of bonding has not been fully understood.

The basis of the process is the raw rubber vulcanization onto metallic surface, which is coated by adhesive reactive bonding layer. This process is rather complex as it involves diverse diffusion phenomena, chemisorption and interfacial crosslinking reactions. This process is shown in Figure 14. (20)

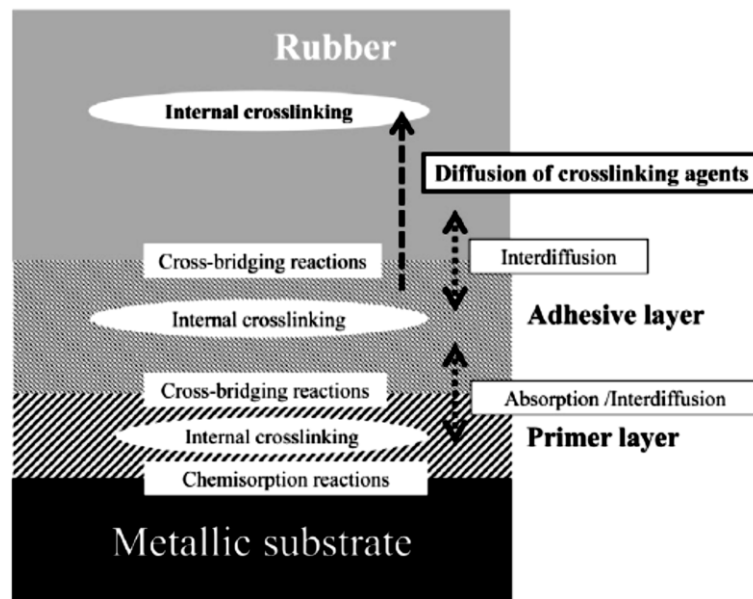


Figure 14 – The Course of reaction and diffusion phenomena for rubber-metal (20)

Various conditions have to fulfill high performance of rubber to metal adhesion. First condition includes internal crosslinking reactions of rubber, primer and adhesive. Second condition refers to efficient chemisorption and cross-bridging reactions generating chemical adhesion at different interfaces. Last condition to achieve high performance rubber to metal adhesion is the generation of decreasing elastic modulus from the metal to bulk of the rubber. (20)

2.5.1 Adhesion mechanism of steel tire cord-rubber

Adhesion between tire cord-rubber is a parameter essential for a correct function of the tire. Good adhesion is ensured by skim compounds based on natural rubber with a high level of tack, sulfur and content of adhesion promoters.

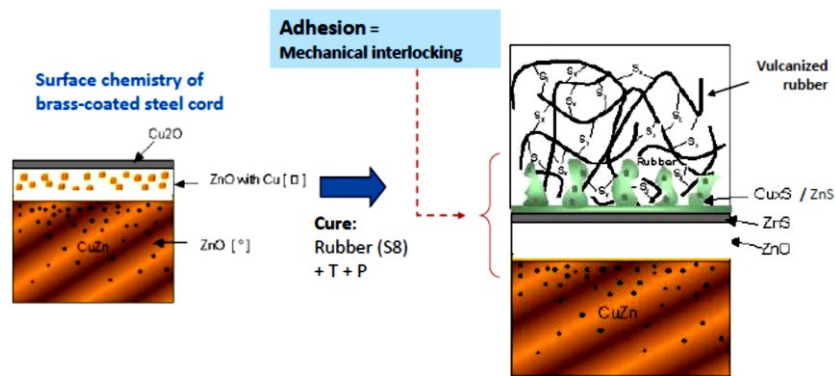


Figure 15 – Mechanism of rubber bonding to steel tire cord (21)

Mechanism is based on the content of Cu_2O and ZnO in surface layers, which subsequently diffuse to the surface and react with rubber molecules. Adhesion is obtained by the growth of dendritic Cu_xS and by mechanical interlocking of rubber phase into these sulfidic structures.

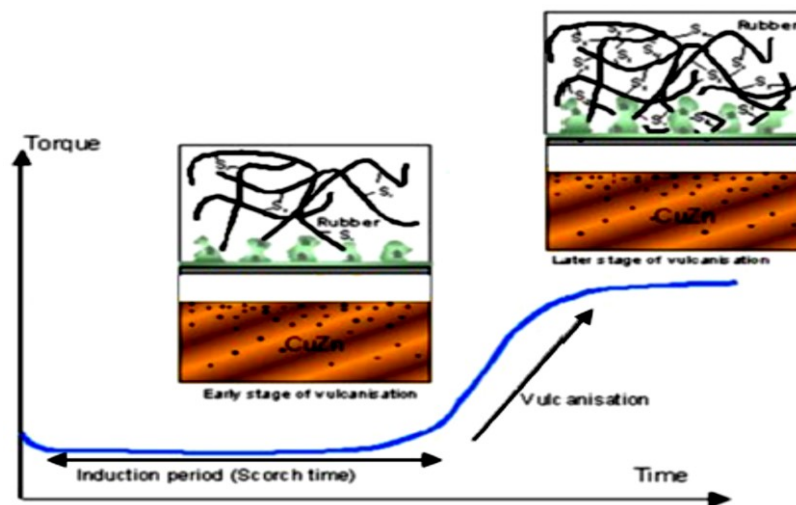


Figure 16 – Vulcanization curve for rubber-metal bonding (21)

Curing process occurs at a certain temperature and pressure. As shown in Figure 16, curing shows a long induction period. Vulcanization begins at a given time and due to it rubber penetrates in cord and crosslinking rubber chains are created. (21)

II. EXPERIMENTAL PART

3 PRINCIPLE OF MEASUREMENT

The experiment is based on the measurement of adhesion force between two rubber samples at a given temperature on dynamic mechanical analyzer with special holding clamp for samples.

As first, setting of temperature, displacement, sizes of sample and type of deformation model was performed. The principle of measurement lies in sensing adhesion force with one sample being fixed and the other oscillating at a set frequency. Adhesion force is measured at maximal displacement, when the sample is in tension, as shown in Figure 17. As a result, the curve of adhesion force rises with time.

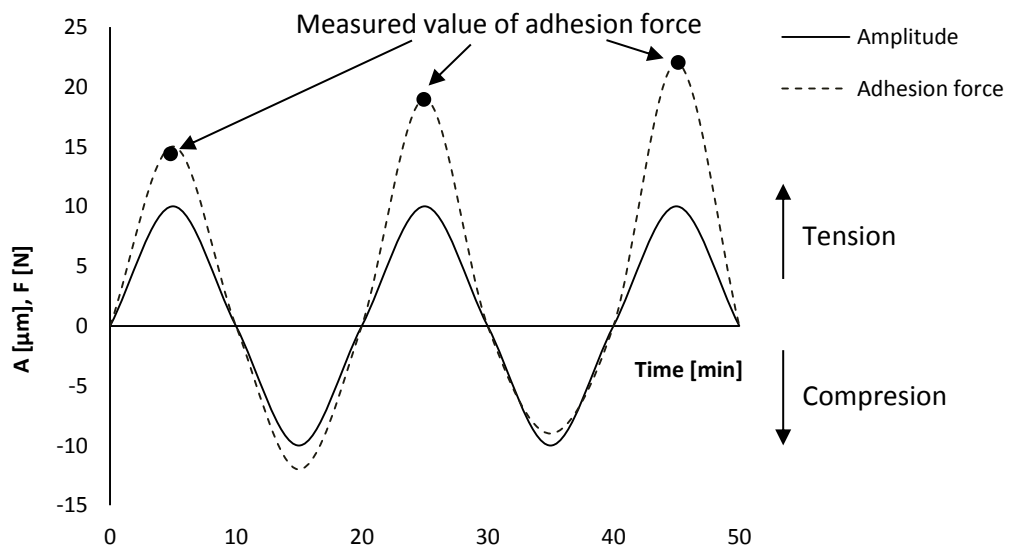


Figure 17 – Principle of measurement

3.1 Dynamic mechanical analyzer (DMA)

Dynamic mechanical analyzer is a multipurpose device which measures mechanical properties of materials as a function of time, temperature and frequency. Measurements could be performed in all standard deformation models, such as bending, tension, shear or compression. DMA is often used to characterize viscoelastic behavior of polymers.

Prepared sample was placed between jaws and fixed. Before the measurement, parameters, such as temperature, frequency and type of deformation were set. Stress-strain curve and vulcanization curve are the examples of measurement results. (22)



Figure 18 – Dynamic mechanical analyzer (DMA) (22)

4 DESIGN OF TESTING SAMPLE

The sample was modeled for measuring on DMA with a special holding clamp. The resulting geometry of specimen has a cylindrical shape with two different diameters. Dimensions are shown in Figure 19.

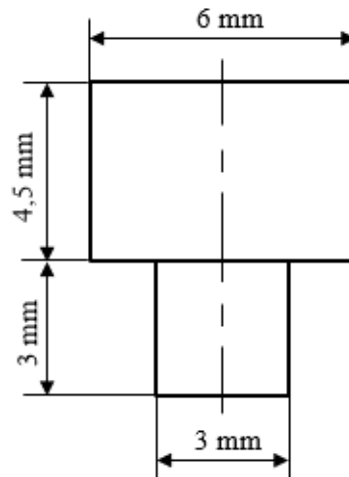


Figure 19 – Dimensions of sample

4.1 FEM analysis

Finite element method (FEM) was used to test the designed sample for the mold dimensioning to prepare samples and a holding clamp for measurement.

The principle of finite element method is based on a division of the profile by means of a finite number of triangular elements of a certain side length. Before starting the analysis of the sample, boundary conditions were defined, including a degree of freedom on the x, y and z axes, network density and applied displacement on the area planned to be tested. These conditions are shown in Figure 20.

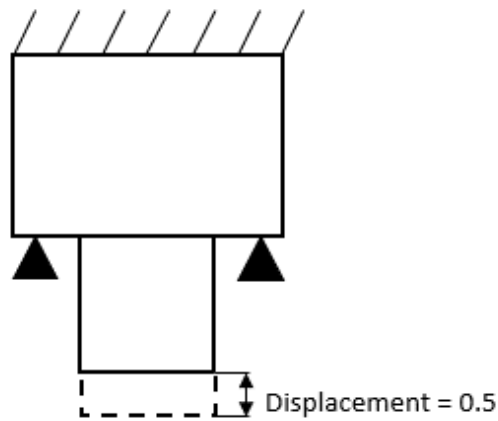


Figure 20 – Conditions for FEM analysis of sample

Ogden material model describing the non-linear stress-strain behavior of complex materials, such as rubbers or polymers, was used for measurement. An uniaxial tensile test examined on uncured rubber was used for this model. The examples of this model are listed in the appendices.

Deformation and stress of the sample needed to mold dimension for the preparation of the samples and a holding clamp for measurement were the results of this testing. They are shown in Figure 21.

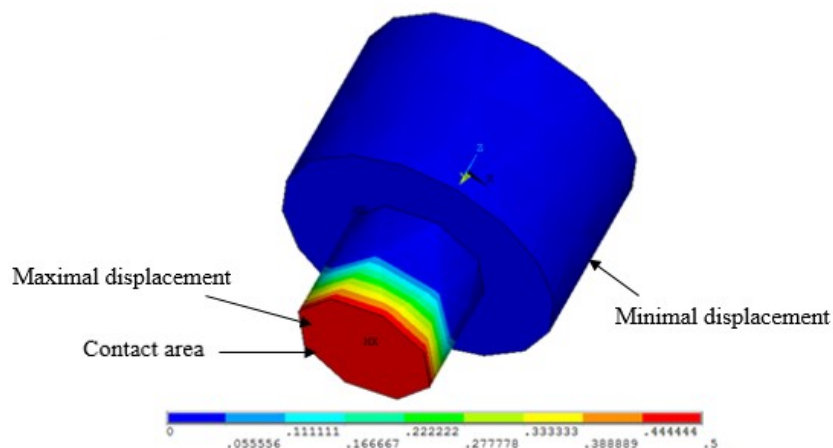


Figure 21 – Displacement of sample on the y-axis

The correct figures are gained if the maximal displacement is within the area where the samples are in the contact and also if other areas are minimally deformed and displaced. These requirements are met as shown in Figure 21.

4.2 Mold for pressing

Mold for the samples pressing has been designed in program CATIA V5. Afterwards, manufacturing drawings, which are listed in appendices, were prepared. Figure 22 depicts a model of the mold designed in CATIA V5.

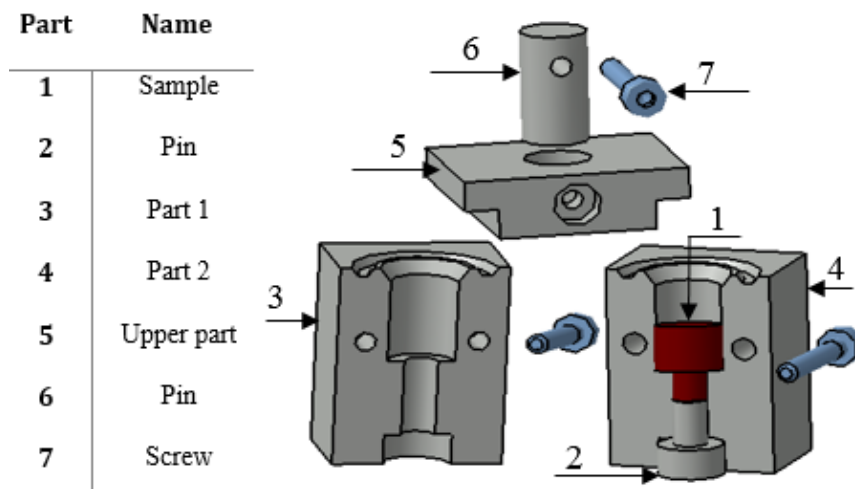


Figure 22 – Mold for pressing of sample in CATIA V5

Real mold with the prepared sample is shown in Figure 23. The samples for measurement were prepared by pressing at the temperature of 50 °C for 30 seconds.



Figure 23 – Mold with prepared sample

4.3 Design of the holding clamp of sample for current testing equipment

It was necessary to design a new holding clamp of the sample, because the existing holding clamp is not appropriate. Then, manufacturing drawings listed in appendices were prepared. This clamp has been designed in CATIA V5 and is shown in Figure 24.

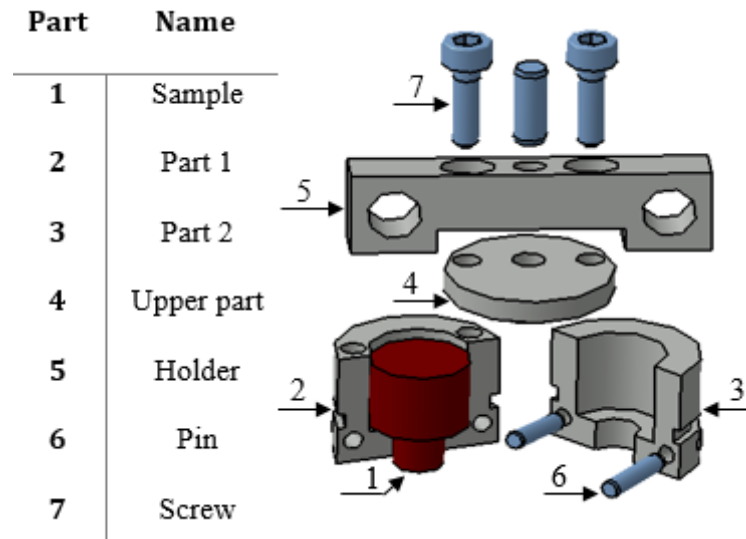


Figure 24 – Holding clamp of sample in CATIA V5

Real holding clamp with the sample is shown in Figure 25. The sample was fixed between two parts of a holding clamp and then the entire assembly was placed into DMA.



Figure 25 – Holding clamp with sample

5 MANUFACTURING OF RUBBER COMPOUNDS

Rubber compounds were prepared by two-step mixing. In the first step mixing of rubber with carbon black was performed in internal kneader Banbury mixer for 7 minutes. Remaining ingredients were mixed in twin cylinder Farrel G-2603 150 x 330 mm for 8 minutes in the second step. Thus, four rubber compounds varying in a type of rubber were prepared. The composition of compounds is shown in Table 4.

Table 4 – Composition of compounds in parts per hundred of rubber (phr)

| Ingredient | NR | BR | SBR | EPDM |
|---------------------|-----------|-----------|------------|-------------|
| NR | 100 | - | - | - |
| BR | - | 100 | - | - |
| SBR | - | - | 100 | - |
| EPDM | - | - | - | 100 |
| Carbon black | 50 | 50 | 50 | 50 |
| Zinc oxide | 3 | 3 | 3 | 3 |
| Stearin | 1 | 1 | 1 | 1 |
| CBS | 2,5 | 2,5 | 2,5 | 2,5 |
| IPPD | 1,5 | 1,5 | 1,5 | 1,5 |
| Sulfur | 1,7 | 1,7 | 1,7 | 1,7 |

6 CHARACTERIZATION OF RHEOLOGICAL PROPERTIES

Rheological properties of prepared rubber compounds were determined by rheometer MDR3000. This device is used to measure viscoelastic properties of polymers and rubber compounds.

MDR3000 is a rheometer containing oscillating rotor inside the chamber into which the sample of compound is placed. The principle is based on measuring the torque, which is induced by constant frequency. Dependence of torque on time expressed by vulcanization curve is gained as a result. It is possible to determine parameters, such as scorch safety (t_2), cure time (t_{90}), maximal torque (M_H) and minimal torque (M_M).



Figure 26 – Rheometer MDR3000 (23)

Testing of prepared rubber compounds were performed at the temperature of 150 °C. The compound sample was placed between the foils and inserted into the chamber. After reaching needed temperature, measurement was launched.

Table 5 – Rheological parameters of prepared rubber compounds

| Compound | M_M [dNm] | M_H [dNm] | t_2 [min] | t_{90} [min] |
|----------|-------------|-------------|-------------|----------------|
| NR | 2.86 | 25.02 | 1.19 | 2.85 |
| BR | 4.91 | 36.75 | 1.69 | 3.56 |
| SBR | 2.86 | 28.98 | 2.95 | 6.21 |
| EPDM | 4.54 | 22.20 | 2.95 | 15.41 |

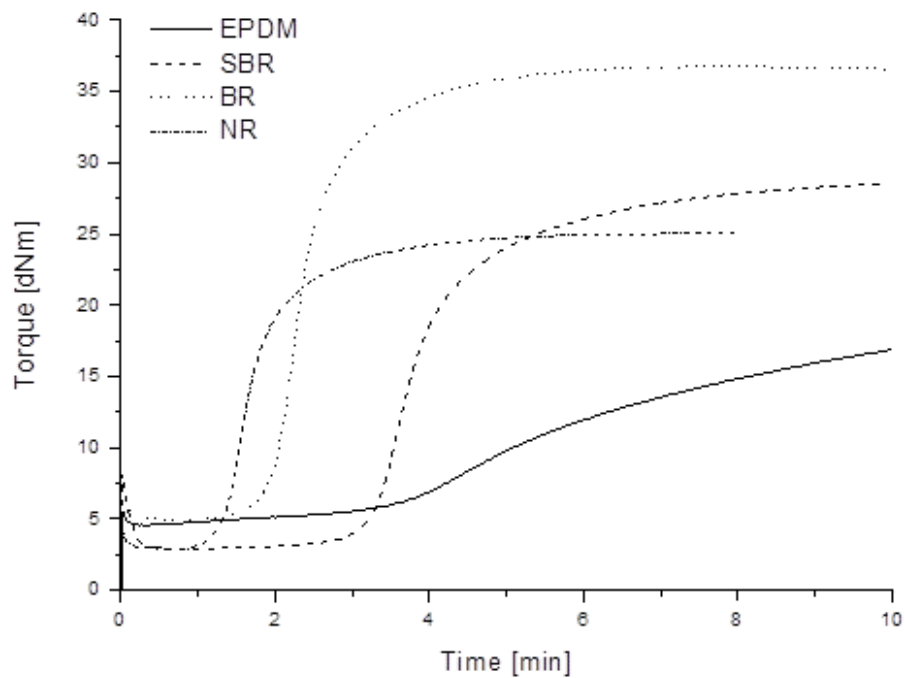


Figure 27 – Curing curves of prepared rubber compounds

Measurement results of rheological parameters show that natural rubber compound has the shortest scorch safety and vulcanization is the fastest. Butadiene rubber compound performs very similar properties, but the maximal module is the highest of all compounds. The time t_{90} is the highest for ethylene propylene diene compound as vulcanization of this compound should be accomplished by using peroxides.

7 MEASUREMENT OF ADHESION FORCE BETWEEN RUBBER-RUBBER

Measurement of curing was performed on DMA equipment with using the designed holding clamp and as type of deformation tension load was used. After heating of the measuring chamber to the needed temperature, prepared samples were fixed in the holding clamp and clamped into the equipment.

Table 6 – Measurement parameters

| Parameter | Value |
|---------------------|--------------|
| Type of deformation | Tension load |
| Temperature | 150 °C |
| Frequency | 1 Hz |
| Time | 15 minutes |
| Amplitude | 10 μm |

Samples pressed from prepared rubber compounds were used for the curing measurement. First the samples from the same compound were measured. Afterwards, various combinations of the samples listed in the table 7 were examined. Due to the large number of sample combinations, only combinations highlighted in bold are described in the next part of the thesis.

Table 7 – Combinations of samples used for measurement

| Combination of samples | Type of samples | Combination of samples | Type of samples |
|------------------------|-----------------|------------------------|-----------------|
| 1. | NR-NR | 6. | NR-SBR |
| 2. | BR-BR | 7. | NR-EPDM |
| 3. | SBR-SBR | 8. | BR-SBR |
| 4. | EPDM-EPDM | 9. | BR-EPDM |
| 5. | NR-BR | 10. | SBR-EPDM |

7.1 Measurement of adhesion force between NR-NR samples at different temperatures (natural rubber)

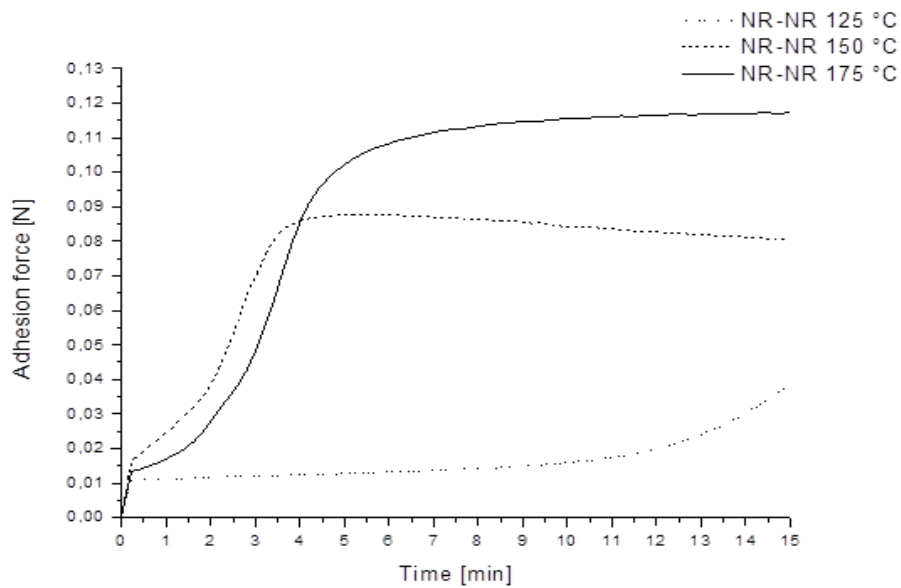


Figure 28 – Dependence of adhesion force on time for NR-NR samples

Measurement of NR samples at different temperatures show that temperature significantly affects the course of adhesion force. The curves follow a similar course typical for vulcanization curve of natural rubber except the curve at 125 °C.

The scorch safeties at the temperatures of 150 °C and 170 °C are very similar, but maximal adhesion force is higher at 175 °C. The curve at 150 °C expresses a faster increase of adhesion force at the beginning of measurement than the curve at 175 °C due to different initial distances between the samples. The course of curves at the end of measurement shows that adhesion forces at 125 °C and 175 °C rise but the adhesion force at 150 °C performs the opposite behavior already during testing. Value of scorch safety for 150 °C are listed in table 9.

7.2 Measurement of adhesion force between SBR-SBR samples

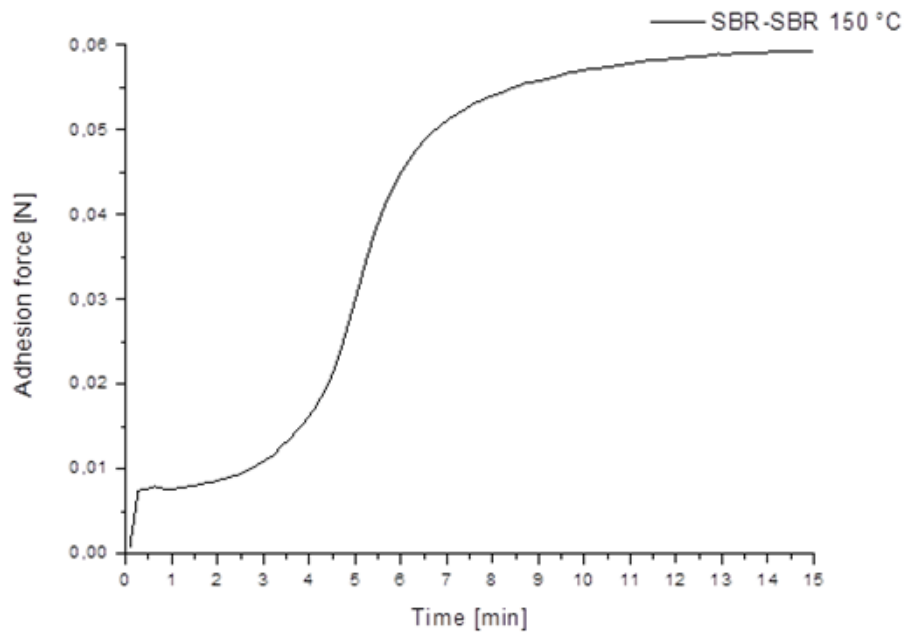


Figure 29 – Dependence of adhesion force on time for SBR-SBR samples

In this experiment, curing has been measured by adhesion force dependent on time, while the result of measuring rheological properties using a rheometer is a dependence of torque on time. As shown in Figure 29, the final curve maintains a similar course as a typical vulcanization curve for styrene butadiene rubber.

The difference between these two types of measurement is the scorch safety that is significantly shorter by means of measuring adhesive force. This may be caused by setting a significantly small initial distance between the samples. After overcoming the scorch safety of compound, the adhesion force soars. At the end of the measurement, the curve has been still rising, which means that the compound has not reached 100 % conversion.

7.3 Comparison of rheological properties measured by rheometer and DMA

One of the aims of this work was to compare rheological properties measured by different devices. Measurements have been performed at 150 °C for 15 minutes. Dependence of adhesion force on time is the result if using dynamic mechanical analyzer and if rheometer MDR3000 were used, dependence of torque on time has been obtained. The final values are stated in Table 8 and 9.

a) Rheometer MDR3000

Table 8 – Rheological parameters of prepared compounds

| Compound | M_M [dNm] | M_H [dNm] | t_2 [min] | t_{90} [min] |
|----------|-------------|-------------|-------------|----------------|
| NR | 2.86 | 25.02 | 1.19 | 2.85 |
| BR | 4.91 | 36.75 | 1.69 | 3.56 |
| SBR | 2.86 | 28.98 | 2.95 | 6.21 |
| EPDM | 4.54 | 22.20 | 2.95 | 15.41 |

b) Dynamic mechanical analyzer (DMA)

Table 9 – Rheological parameters of prepared compounds

| Compound | F_{MIN} [N] | F_{MAX} [N] | t_2 [min] | t_{90} [min] |
|----------|---------------|---------------|-------------|----------------|
| NR | 0.002 | 0.117 | 0.17 | 4.50 |
| BR | 0.017 | 0.106 | 0.94 | 5.34 |
| SBR | 0.001 | 0.059 | 0.16 | 7.65 |
| EPDM | 0.034 | 0.084 | 0.70 | 12.91 |

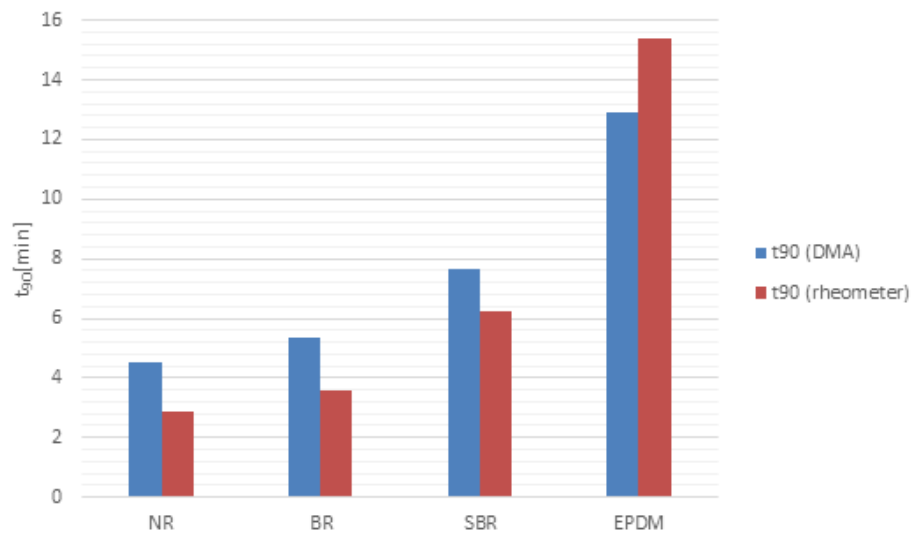


Figure 30 – Comparison of time t_{90} for DMA and rheometer

Results displayed in Figure 30 show that the time t_{90} is very similar for all compounds. Longer times have been reached using DMA with the exception of EPDM which could be explained by continuing curing of the compound after the end of the measurement. The results may also be affected by the size of curing area. Longer times regarding DMA could also be influenced by different initial distance between the samples, which cannot be set precisely.

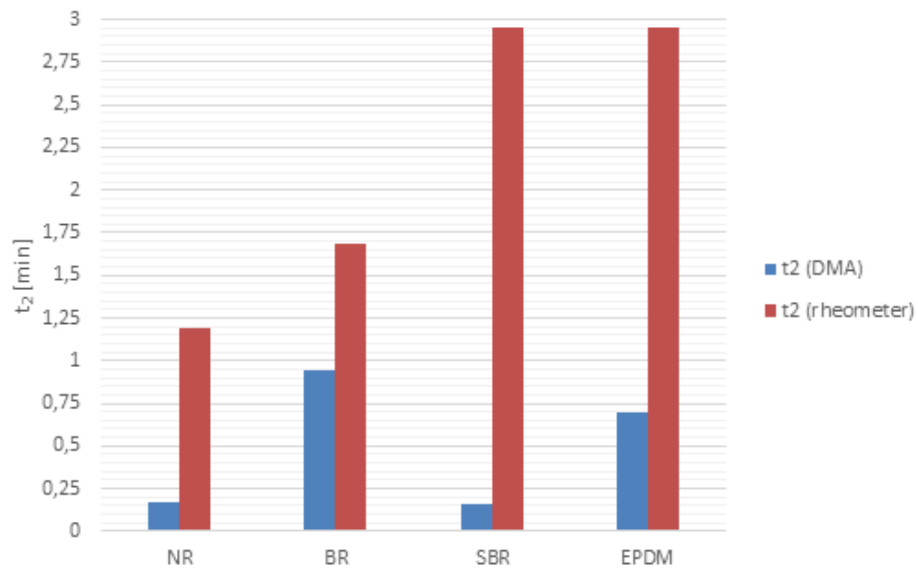


Figure 31 – Comparison of time t_2 for DMA and rheometer

The scorch safety is significantly bigger for all compounds on rheometer. The reasons of short times t_2 may be the amount of the material for testing, the size of curing area or premature curing.

CONCLUSION

Presented master's thesis deals with the description and comparison of curing kinetics of rubber measured by using two different devices. It also focuses on the development of the method clarifying complete kinetics process between two rubber parts.

All points of the assignment have been fulfilled. Theoretical part describes a curing process and associated issues. Theoretical basis for the measurement methodology and design of necessary components for the experiment on basic FEM analysis of designed sample have been established. Further, rubber compounds were prepared and their rheological properties essential to understand the behaviour of compounds determined. Finally, the analysis, evaluation and comparison of results were performed.

Results from DMA measurement have proved that temperature significantly influences the course of curing between two rubber parts. The curves follow a similar course typical for curing curves of rubber compounds from rheometer. Comparison of rheological properties from DMA and rheometer has shown that times t_{90} are very similar. On the other hand, times t_2 from DMA are significantly shorter. However, results from DMA may not be accurate as the parameters, such as an initial distance between the samples or time of the sample in the heated chamber, may distort the resulting data.

Analysis of curing between two rubber parts by this method is highly promising; however, it is significantly essential to improve settings and the measurement itself to achieve reliable data.

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LIST OF ABBREVIATIONS

| | |
|-------------------|---|
| BR | butadiene rubber |
| CaCO ₃ | calcium carbonate |
| CBS | N-cyclohexyl-2-benzothiazolesulfenamide |
| CR | chloroprene rubber |
| Cu ₂ O | copper oxide |
| CuxS | copper sulphide |
| DCP | dicumyl peroxide |
| DMA | dynamic mechanical analyzer |
| dNm | deci newton meter |
| EPDM | ethylene propylene diene monomer |
| FEM | finite element method |
| FKM | fluoroelastomer |
| IIR | butyl rubber |
| IPPD | N-isopropyl-N'-phenyl-p-phenylenediamine |
| M _H | maximal torque |
| M _M | minimal torque |
| MBS | N-oxydienthylene-2-benzothiazolesulfenamide |
| MBT | 2-mercaptobenzothiazole |
| MDR | moving disc rheometer |
| MBTS | dibenzothiazole disulfide |
| NR | natural rubber |
| ODR | oscillating disc rheometer |
| phr | parts per hundred parts of rubber |
| R | rate of cure |

| | |
|-----------------|---|
| RPA | rubber process analyzer |
| SBR | styrene butadiene rubber |
| S ₈ | eight-membered ring of sulfur molecule |
| TBBS | N-tert-Butyl-2-benzothiazolesulfenamide |
| t ₂ | scorch safety time |
| t ₉₀ | cure time |

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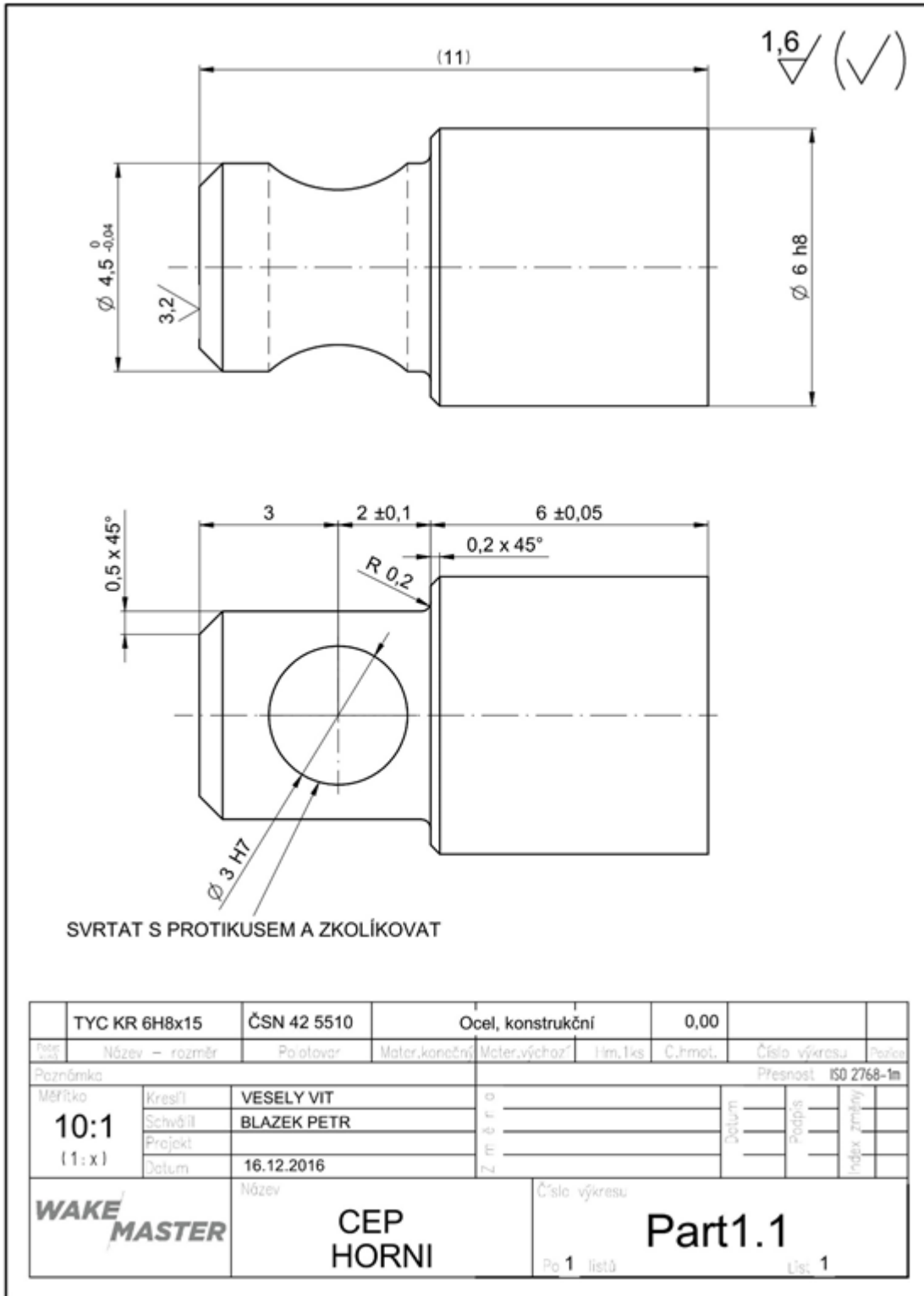
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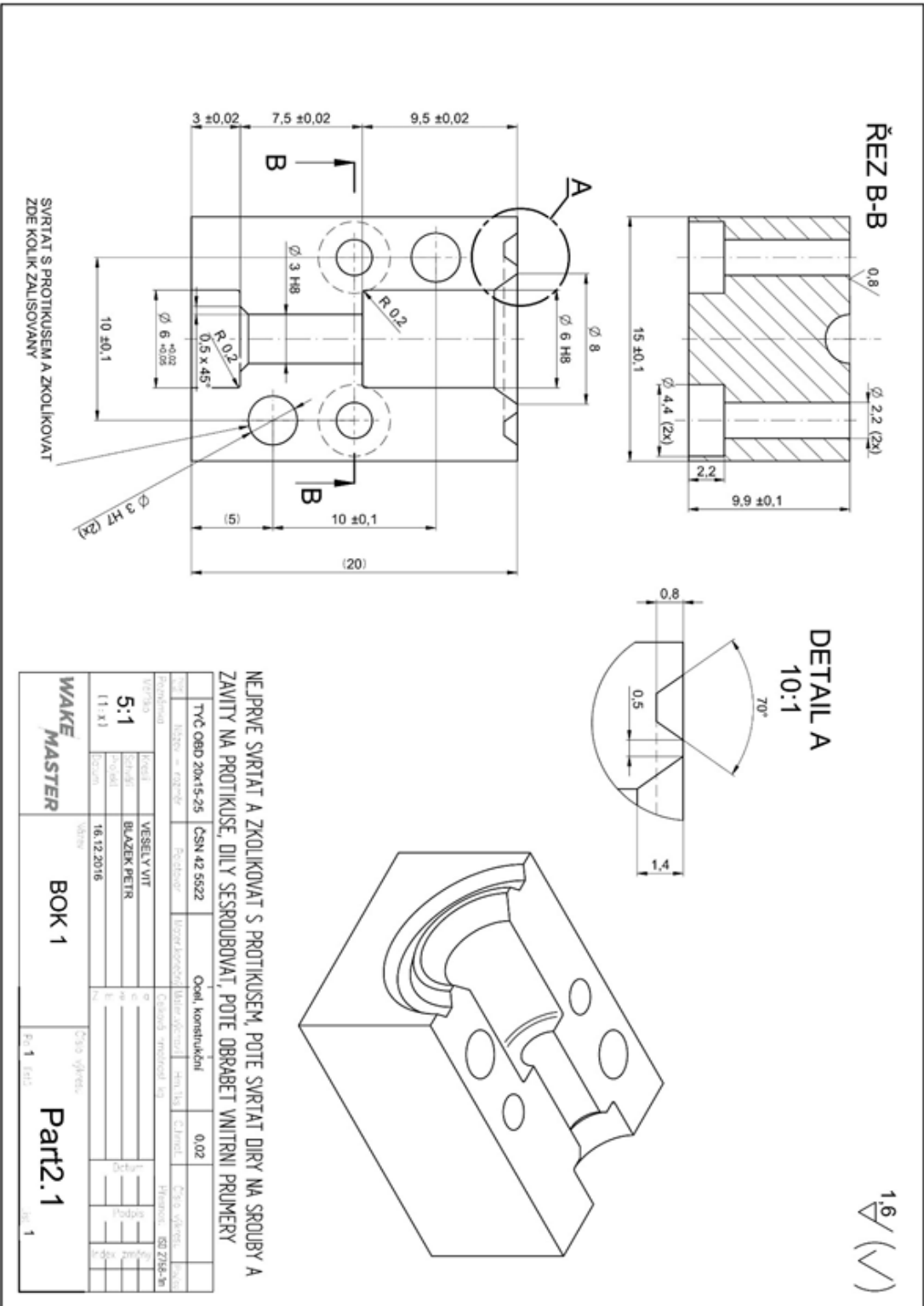
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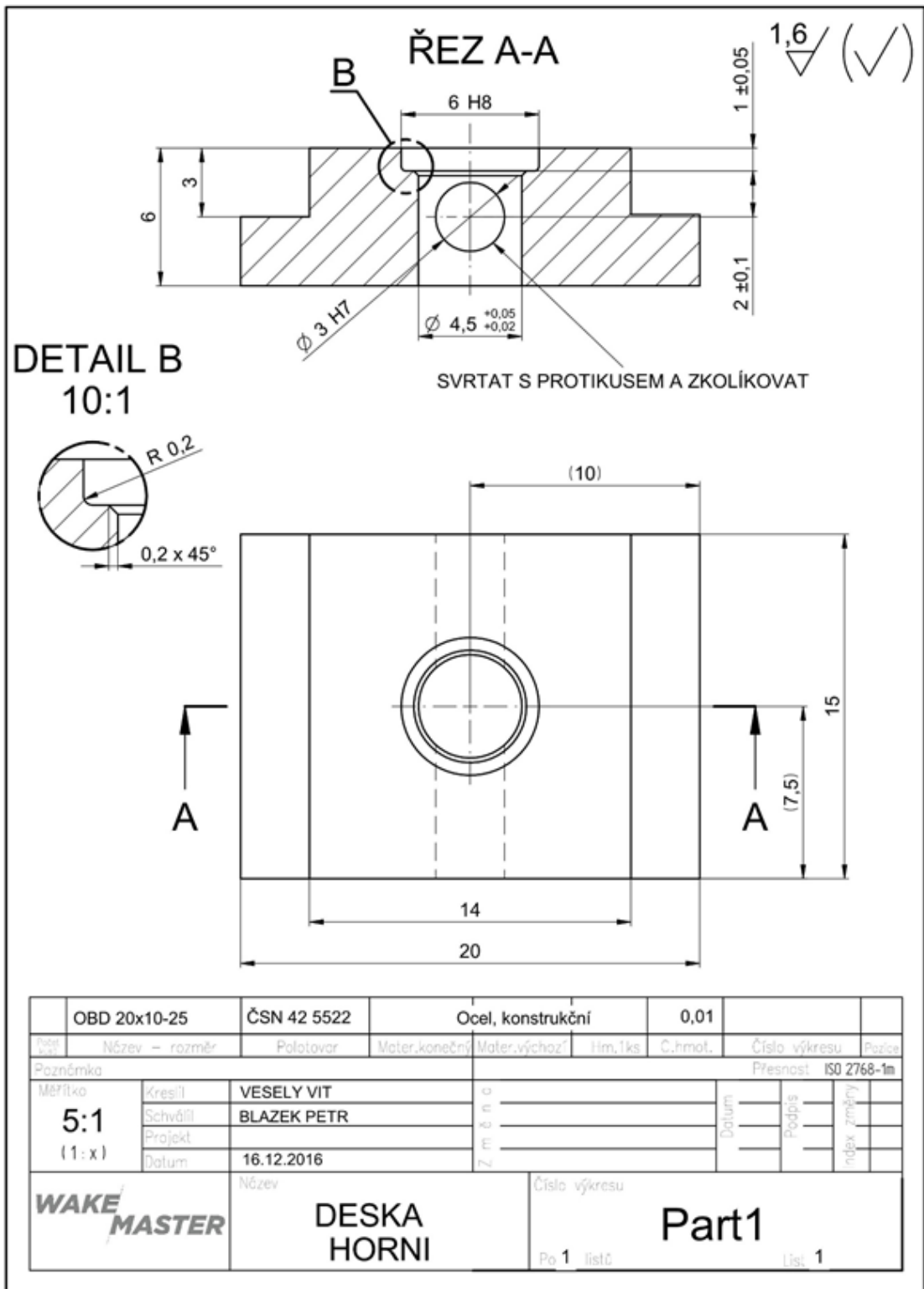
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APPENDIX P I: MANUFACTURING DRAWINGS OF MOLD FOR PRESSING



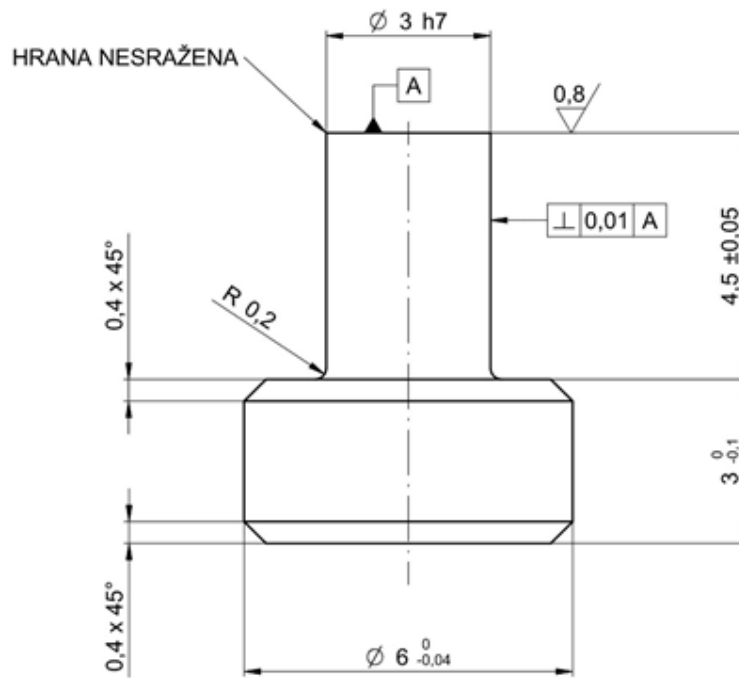


Appendix 2 – Part 1 (mold)



Appendix 4 – Upper part (mold)

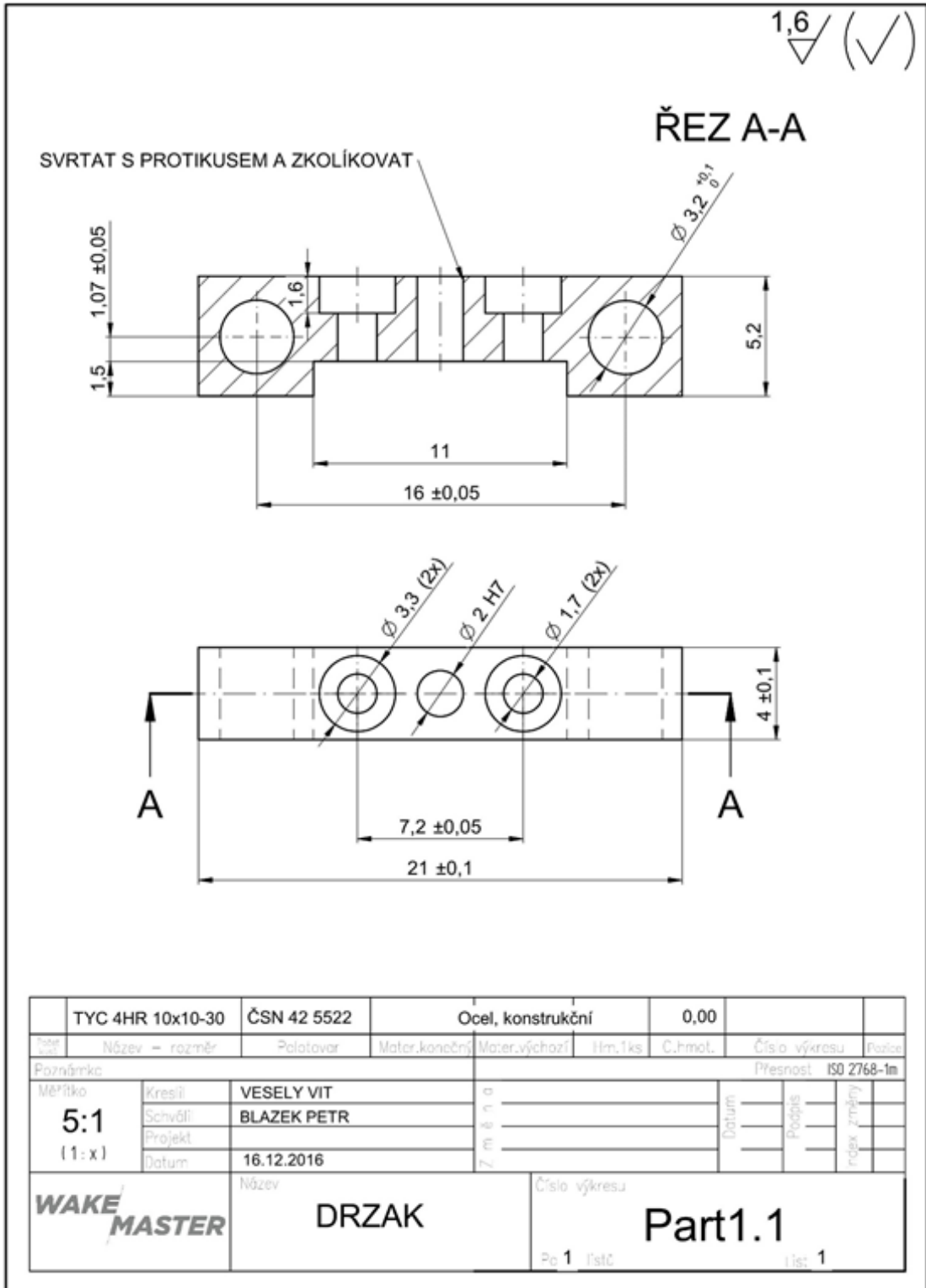
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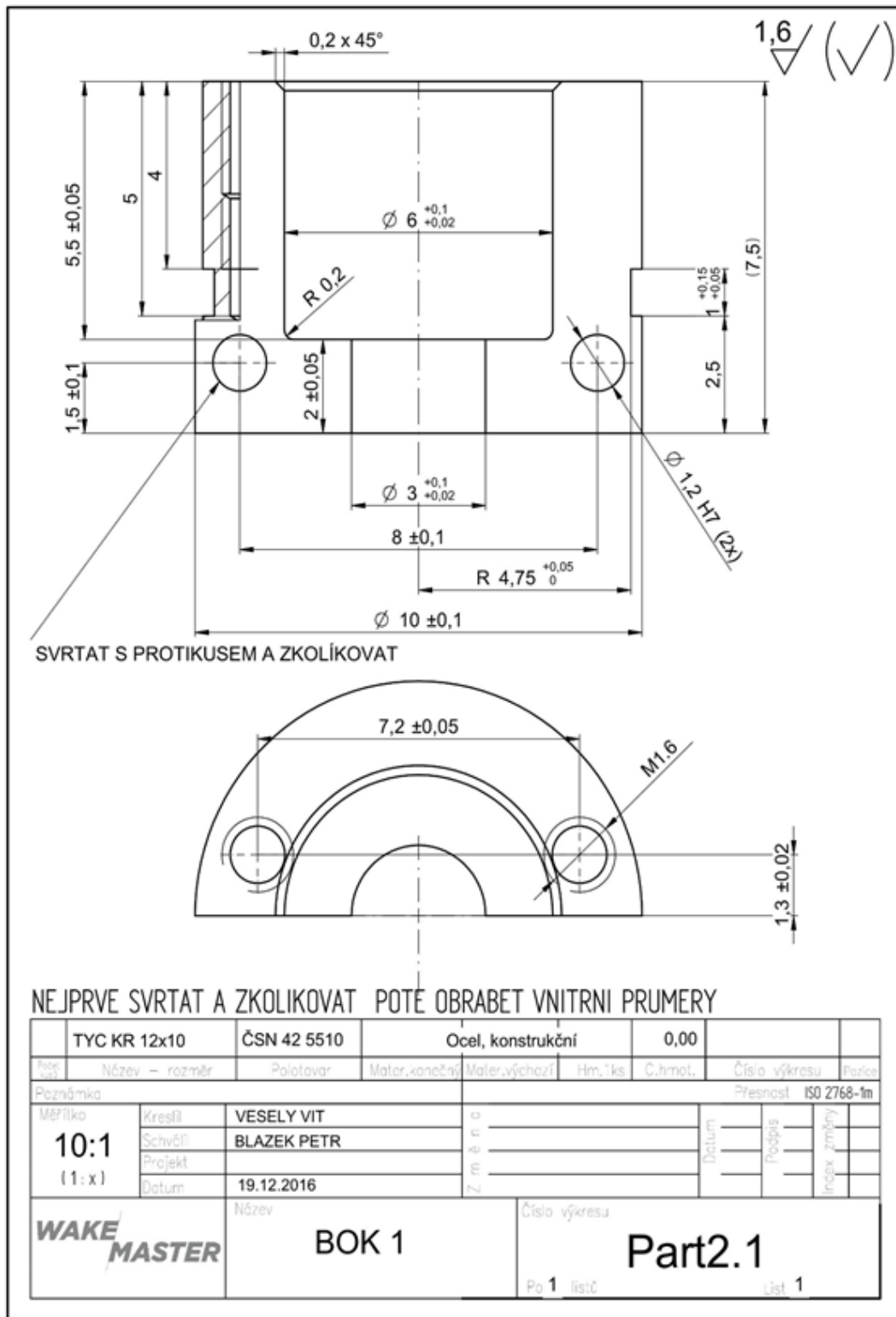
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| Poznámka | | | | | | | Přesnost | ISO 2768-1m |
| Měřítko | Kreslil | VESELY VIT | Změna | | Datum | Proces | Index změny | |
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| (1:x) | Projekt | | | | | | | |
| | Datum | 16.12.2016 | | | | | | |
| WAKE MASTER | | Název | CEP | | Číslo výkresu | | | |
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Appendix 5 – Pin 1

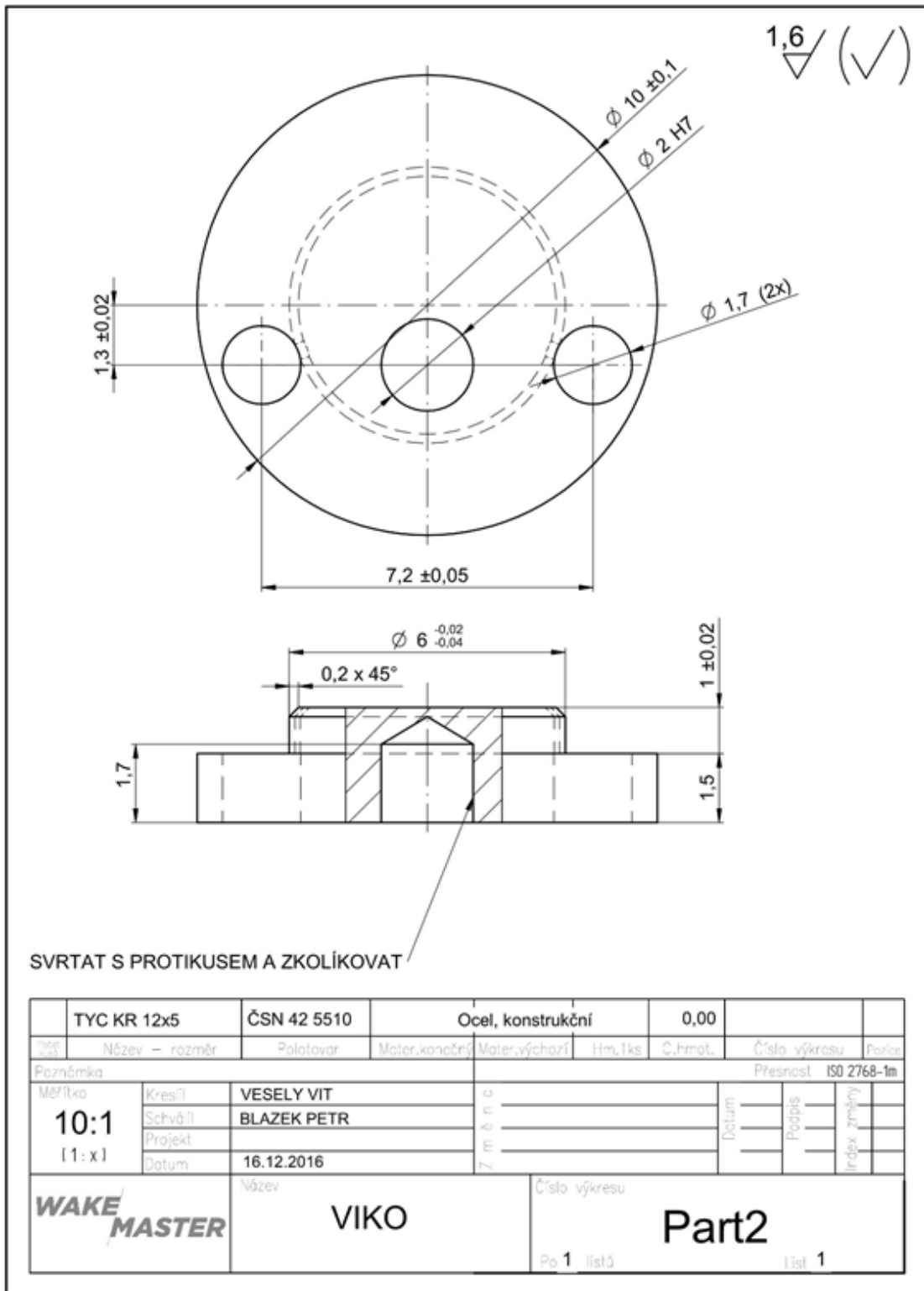
APPENDIX P II: MANUFACTURING DRAWINGS OF HOLDING CLAMP



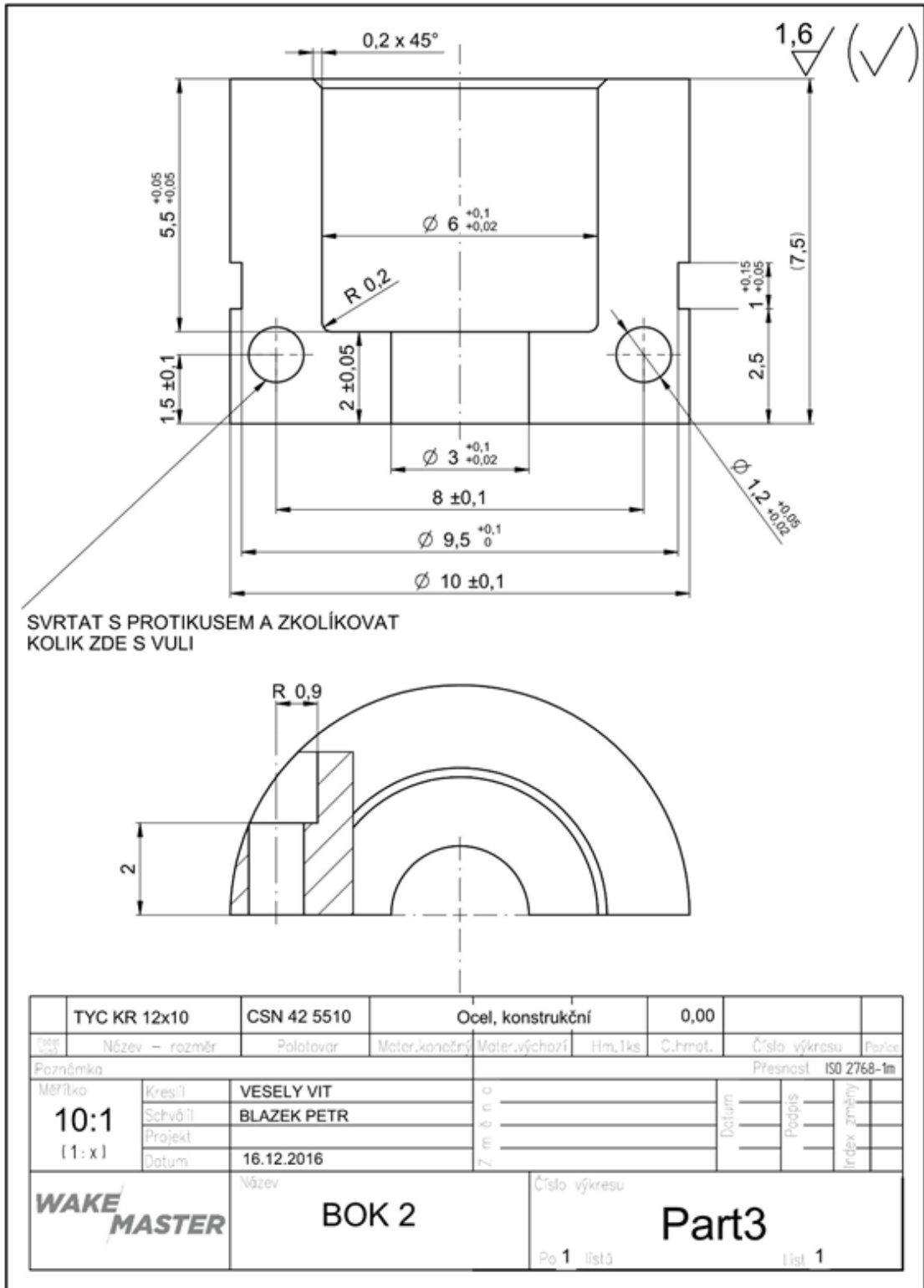
Appendix 7 – Holder



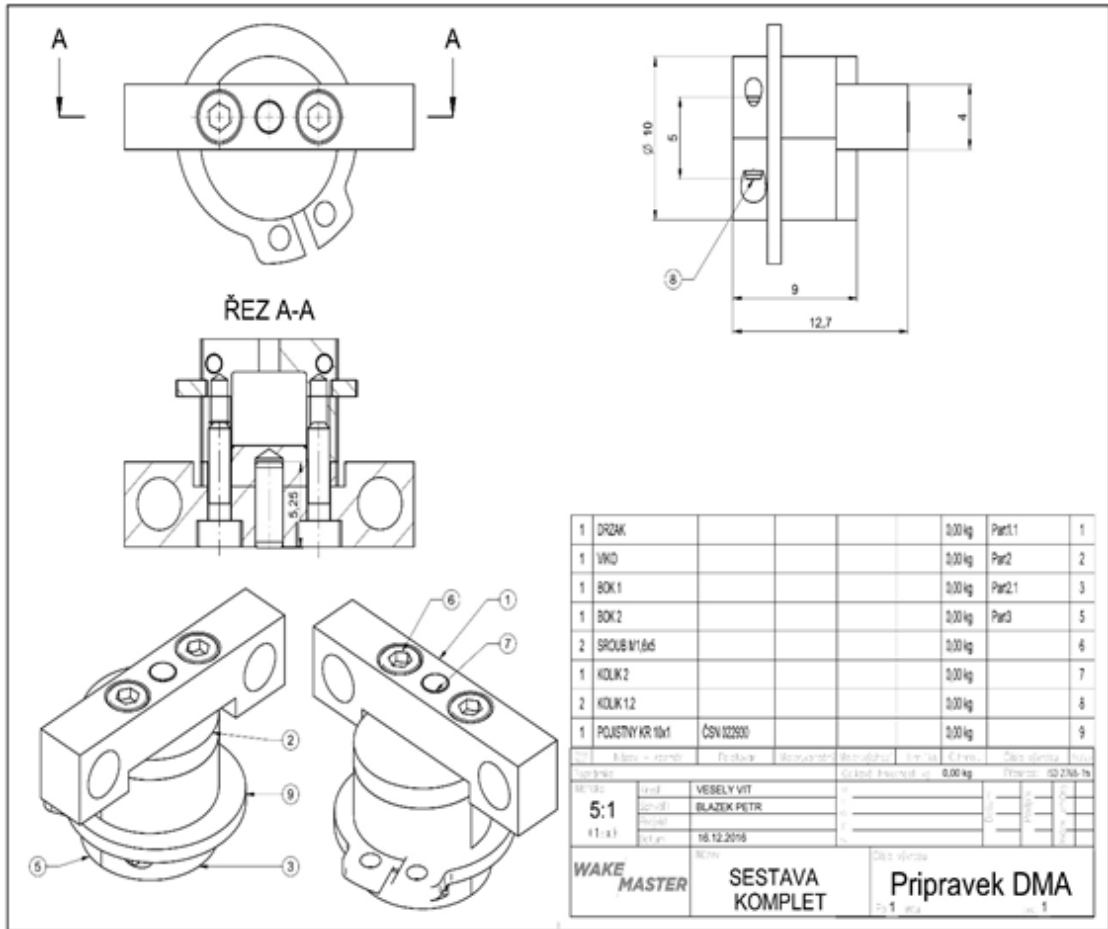
Appendix 8 – Part 1 (holding clamp)



Appendix 9 – Upper part (holding clamp)



Appendix 10 – Part 2 (holding clamp)



Appendix 11 – Holding clamp

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TBFT,FSET,1,HYPER,OGDE,3

NLGEOM,ON

ET,1,SOLID98

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KEYOPT,1,5,0
|
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VMESH,all

/solu

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DA,2,all
DA,5,UY,0.5

solve

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Appendix 12 – Ogden model