Measuring the micromechanical properties of the coating modified PLA

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ABSTRAKT

Tato práce se zabývá měřením mikrotvrdosti modifikovaného PLA-Polylactid acid.V teoretické práci jsou popsány metody měřenítvrdosti a mikrotvrdosti různými způsoby. Dále jsou popsány modifikace polymer a jejich struktura. Praktická část zahrnuje přípravu vzork u jeho modifikace a následné měření, nakonec statistické zpracování hodnot po měření.

Klíčováslova: Mikrotvrdost, PLA, Modifikace polymerů

ABSTRACT

The thesis deals with measurement of modified PLA-Polylactid acid microhardness. In theoretical part are described methods of measuring hardness and microhardness in different ways. Further are described modifications of polymers and its structure. Practical part includes test sample preparation, modification and measurements, eventually statistical evaluation measured values.

Keywords: Microhardness, PLA, Polymer modification

ACKNOWLEDGEMENTS

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INTRODUCTION

Aim of this master thesis is measurement of micromechanical properties of coating (surface layer) modified Polylactid acid-PLA. Polymers are nowadays very used for all kinds of applications from sports, home applications to industry.

Bio-based polymers will be in future on top of manufacturing due the lack of fossil fuels, so the industry should focus on decrease cost of manufacturing bio-based polymers. Not all of the biopolymers will have same properties as the polymers from fossil fuels so we should also focus on modification these polymers that the properties can be changed according applications.

Modification of polymers can also change their structure which also influence other properties such as degradation of polymers, more important is effect of structure change for biodegradable polymers due applications for them.

Hardness is one of the basic construction material mechanical properties due that is very often measured, it is defined as resistance against penetration of foreign body. The most common methods for measuring hardness are Brinell, Vickers and Knoop. Main advantages are speed, repeatability and relative simple procedure. We also distinguish tests of macro and microhardness.

DSI-Depth Sensing Indentation is used for measurement of microhardness, which is one of the modern hardness measurement methods. It is required that the total depth of indentation is equal to 10% from the total layer depth. Graphical representation of data shows indentation curve of loading depth-indentation.

In experimental part was chosen PLA later modified by annealing of various temperatures and measured by DSI method at 0,5N, 1N and 5N loads. Measured results are evaluated and compared in diagrams.

I. THEORY

1 POLYMER MATERIALS

The polymers are chemical substances with wide range of properties, polymers contain in molecules mostly carbon atoms, hydrogen, oxygen, nitrogen, chlorine and other elements. Polymers products are in solid state, but in the certain process stage they are in liquid state, which enables them, usually at elevated pressure and temperature, to give various shapes to future product, according anticipated usage.

The polymers are composed of macromolecules that are very large molecules which consist of smaller units, called monomers, with strong covalent bonds they are tightly bonded together. Polymers are divided into two groups. First is group is thermoplastic and second is elastomeric group. Plastics are normally usually hard often also brittle. At elevated temperatures they become plastic and mold. If the change from plastic to solid state is reversible so we call them the thermoplastics. If the change is irreversible is then result of chemical reactions taking place at elevated temperatures, speaking of the thermosets. [1, 11]
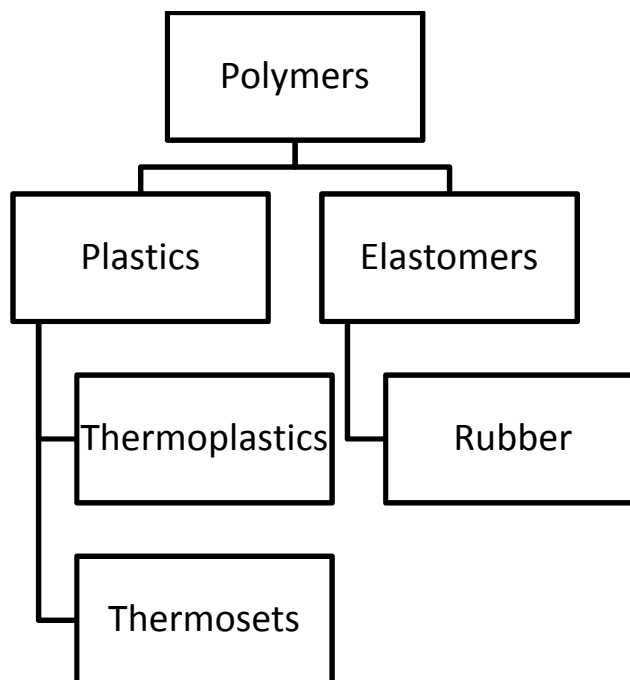

Fig.1 Distribution of polymers [1]

1.1 Structure of polymers

By connecting structure units are formed macromolecular substances, which are done by polyreaction. Each structure unit must have at least two places capable of chemical reaction with other molecules. Capable reaction is for example carboxyl group -COOH or alcohol group –OH. At two reaction places in molecule are molecules capable chemically bond with two neighbor molecules. This gives rise to linear macromolecules in chain form creating linear polymer. Between these flexible chains operates also weak Van der Walls bonds. [3]
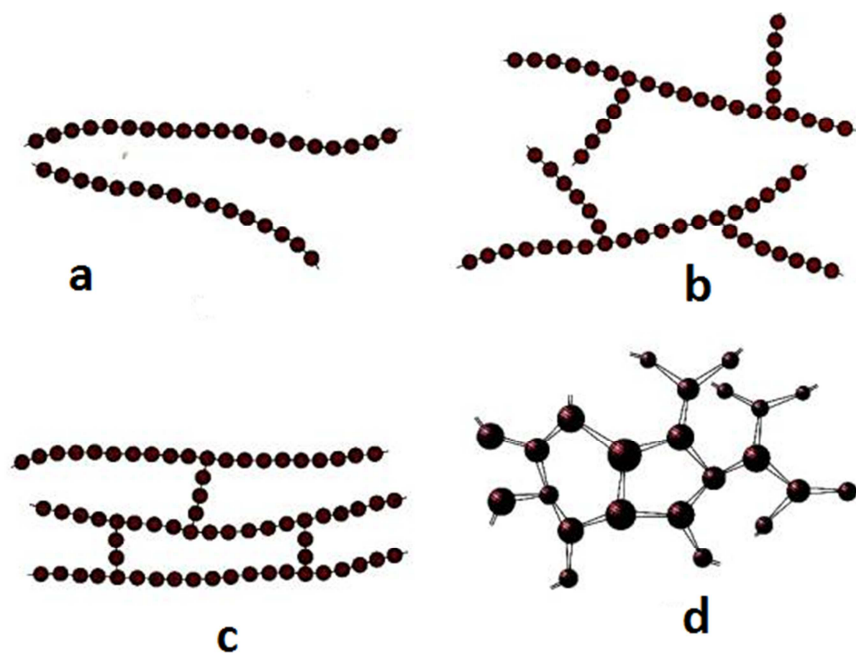
Fig.2 Structure of polymers a) linear; b) branched; c) with crossed links;

d) Cross-linked [3]

The polymers with macromolecules characterized by main chain, which form extended lateral branches, are called branched polymers. Whole structure has lower density than linear polymers. Neighbor polymer chains, which are connected by units bond with strong covalent bond, and are known as polymers with crossed links. Cross-linked polymers include different elastic materials for example natural and synthetic rubber. These polymers have thanks to cross-linked molecules different physical and chemical properties than linear polymers. [1]

The polymers formed by polymerization with more than one monomer type are called copolymers. Monomers can rotate either random or alternately. So it's created different structures of copolymers, random, alternating, static and grafted. [3]
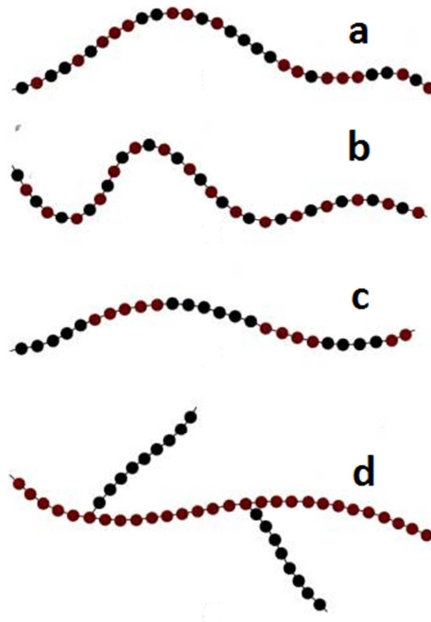
Fig.3 Structure of copolymers a) random;

b) Alternating; c) static; d) grafted [3]

An important concept in the production of polymers is the polymerization degree. It expresses number of repeating basic units (monomers) in molecule chain and solids takes values around hundreds and thousands. Of course all chains do not have same length. Degree of polymerization varies around single value, which is called average degree of polymerization. It is marked by letter n. Degree of polymerization significantly influence properties of specific substance. The higher degree of polymerization (molecule weight) the more is polymer stiffer and more resistant to shocks, but after melting are less formable. [1,3]

Great length of macromolecules is an obstacle to their full crystallization. Yet even polymers we observe crystallization state such that macromolecules are in limited volume regularly arranged. Polymers show a certain degree of order that is defined as crystallization degree, from 40 to 90% and expresses relative quotient of organized areas, located between amorphous areas. But it can never reach 100%, because of that crystalline plastics are indicated as semi-crystalline plastics. PE, PP, PA, PTFE, POM belongs to this group and many others. They are milky, refractive index is higher compared to amorphous polymers and they are characterized by toughness, strength and elastic modulus increases with degree of crystallization. Usability of semi-crystalline plastic is to melt temperature T_m. Lot of polymers, crystallizing from generates so-called spherulites which have spherical shape. [1,3]

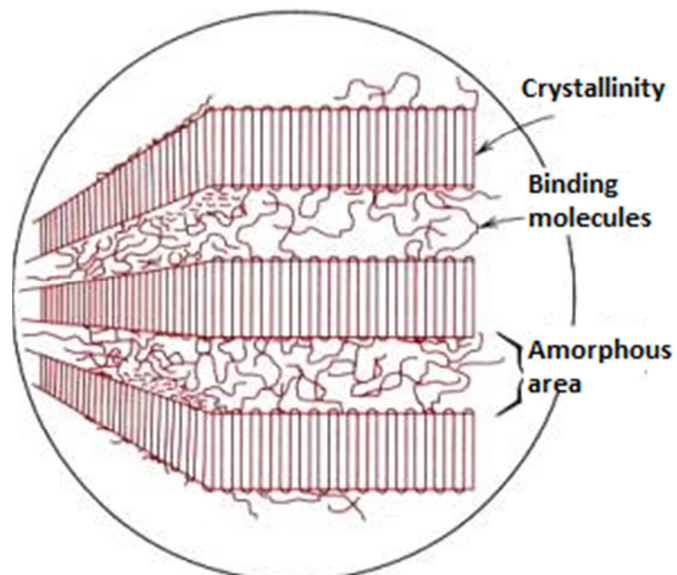*Fig.4 Semi-crystalline polymer* [3]

Amorphous plastics are those in which macromolecules occupies entirely random position. PS, PMMA, PC belongs to this group and many others. They are characteristic by hardness, brittleness; high strength and elastic modulus, due to low refraction index are transparent or according to light transmission pure or translucent. [3]
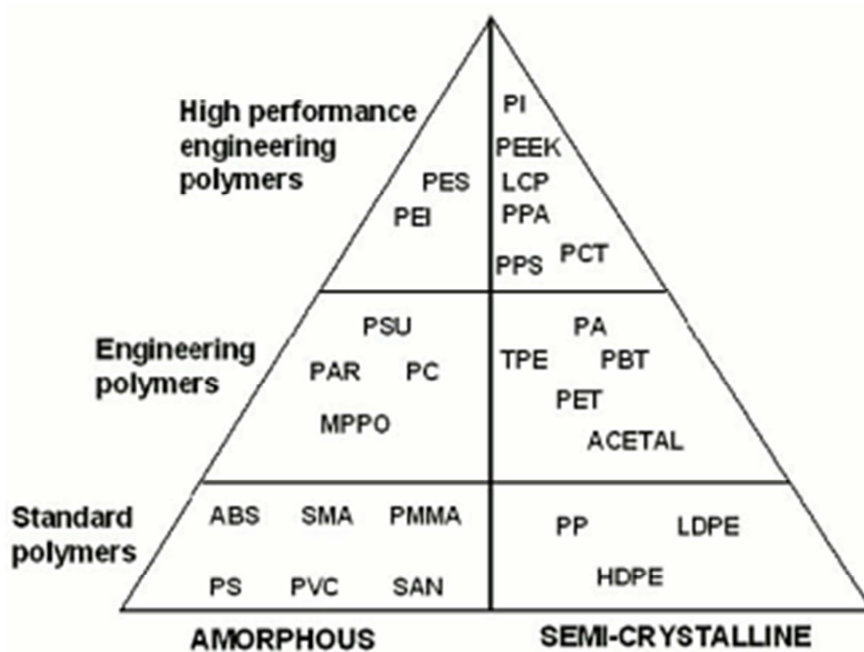

Fig.5 Distribution of polymers [4]

1.2 Bio-based and biodegradable polymers

Since the early 70s the subject of biodegradable polymers caught wide notion, biodegradable polymers experienced a few important stages of development and received extensive investigation from academia and industry. Due to significant portion of plastics in municipal waste, degradable and biodegradable were originally intended to solve problem of landfill, that some landfill space would be freed with biodegradable waste plastic. It is very complicated to merge in product requirements such as great stability of utility properties and quick possible degradation. Main reason of this condition is that intensity of individual environment active effects such as heat, oxygen, solar radiation, humidity and microorganisms on polymer material depends on many factors like season of the year, geographic location, height above sea level and others. Bio based polymers also don't have to mean that they are biodegradable, distributions of biopolymers are shown on fig. 6. [1,5]
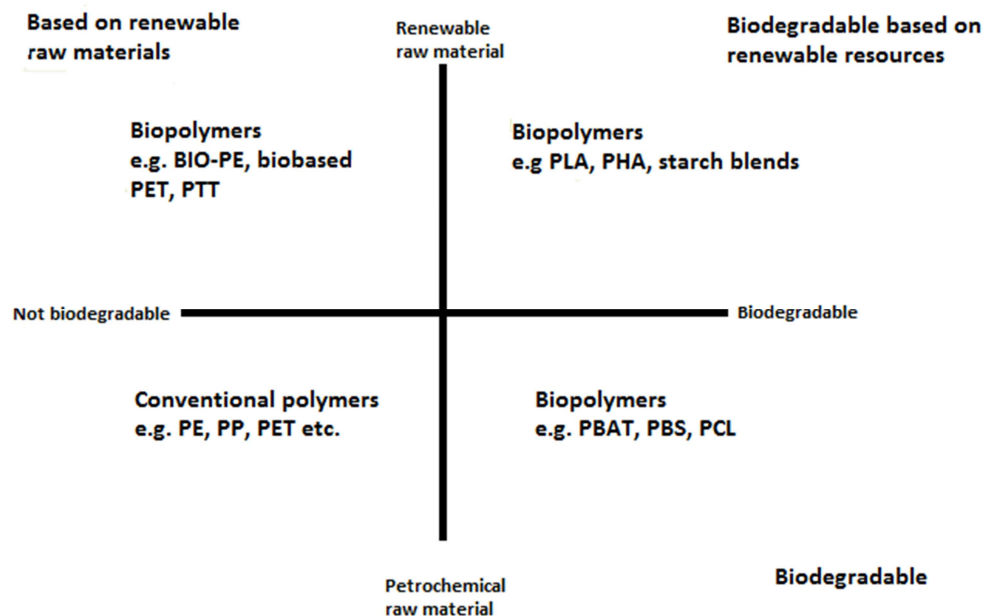
Fig.6 Terminology bio-based plastics

Environment footprint was not considered with first generation of degradable plastic, in priority was focused only on landfill space saving. Lot of these products are based on polyolefins filled with starch or activated with metal oxide or transition melt salt, which only disintegrate into small pieces over time due to biodegradation of starch ingredient or catalyzed photodegradation of the polyolefins. Their application were mostly carrier bags, waste bags for composting or in soil were this thin films disintegrated, starch is decomposed but polyolefin part remain intact to this environment.[1,5]
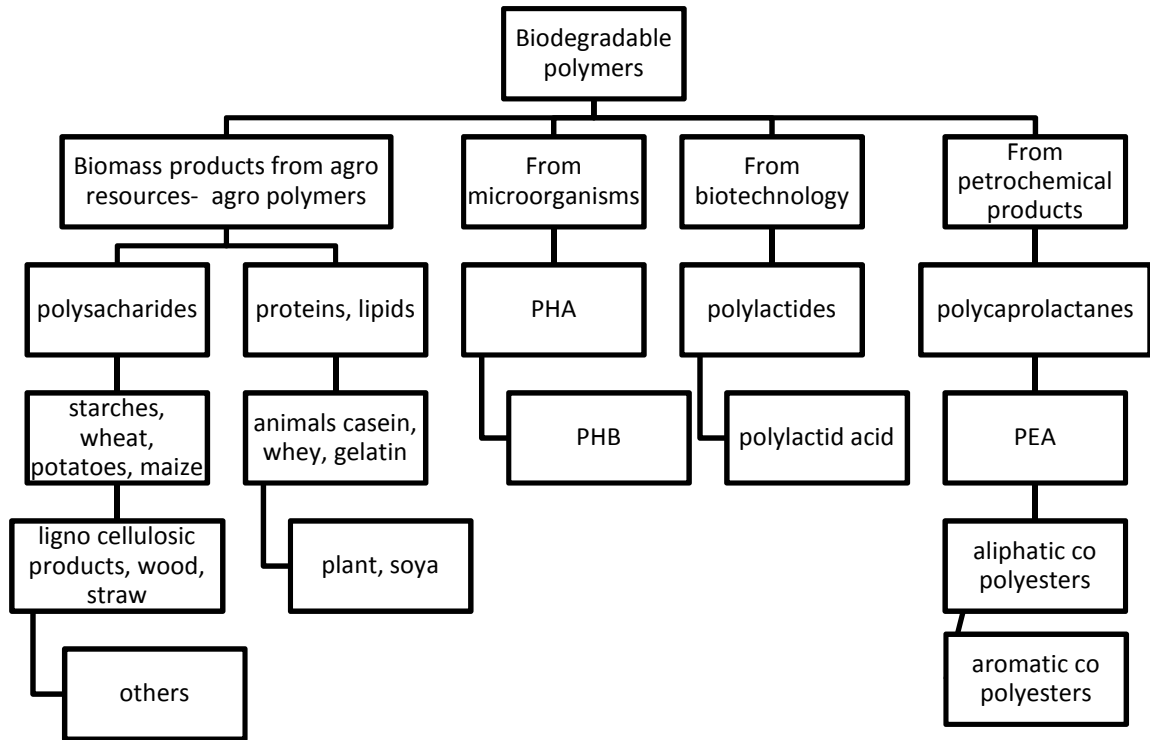
Fig.7 Biodegradable polymers [6]

Two very important biodegradable polymers, which are derived from renewable resources, are polylactid acid- PLA and polyhydroxyalkanoates-PHA. These thermoplastics show mechanical properties and process-ability similar to that of some polymer based on petrol. [1,5]

Advantages

- Biopolymers are recyclable
- Environmentally friendly
- Packaging of biodegradable polymers can be composted

Disadvantages

- Technology to improve fast and efficient production of PHA is still not enough expanded
- Biopolymer production methods are still very costly
- Product quality may be inconsistent and the variable patterns of supply mean price fluctuation and material itself is rather brittle
- Large scale composting facilities will cost a lot of money

1.2.1 PLA

Biodegradable synthetic polyester PLA with its monomer, lactic acid, is derived from natural resources. Lactic acid is made from corn, sugarcane, potatoes and other biomass by bacterial fermentation of carbohydrates. There are three different routes how to synthesize high-molecular-weight PLA: [5,7]

- Direct condensation polymerization
- Azeotropicdehydrative condensation
- Ring-opening polymerization of lactide
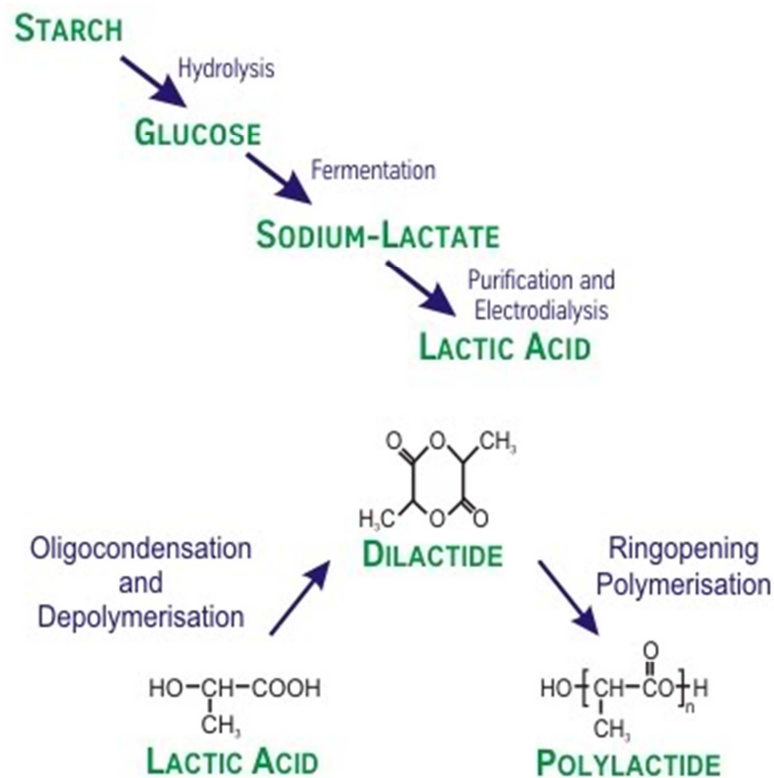
Fig.8 Manufacturing of PLA [8]

Cargill route was last patented route and is the most commonly used method. The least expensive method is direct condensation polymerization, but it can only obtain low-molecular-weight PLA, because it is difficult to remove water completely from the reaction mixture. Well known is PLA for biodegradability and biocompatibility. [5,7]

Thermoplastic polymer can be conveniently processed by existing polymer processing equipment and techniques. Fiber, film, sheet, and 3D articles by fiber drawing, film blowing, extrusion and injection molding can be processed from PLA. The market share is

gradually gained by PLA, with the continuous drop of resin price. PLA is suitable for bio-degradable packaging, such as bottles, food containers and wrappers for its clarity. Food service ware, lawn and food waste bags, coatings for paper and cardboard, and the fibers for clothing, carpets, sheets and towels, and wall coverings, for all this is also used PLA. [5,7]

Biomedical applications for PLA are sutures, stents, prosthetic materials, dialysis media and drug delivery devices. Through a two-stage process primarily by hydrolysis is PLA degraded. PLA reduces its molecular weight by first random chain scission of the ester groups. Temperature, pH value and environment moisture level, on all this depends chain scission speed. With the reduction of its molecular weight embrittlement of the polymers occurs. By microorganisms, yielding carbon dioxide, water and humus is metabolized low-molecular-weight PLA. [5,7]
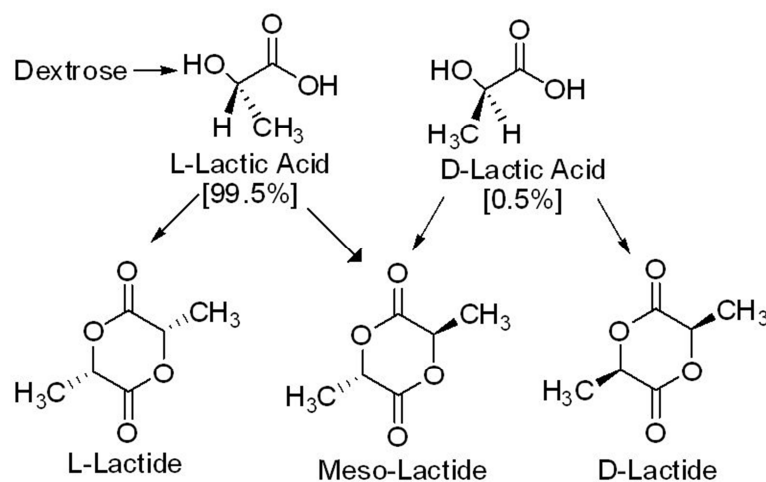
Fig.9 PLA types [9]

PLA properties can be quite different due to presence of the pendent methyl group on the alpha carbon atom. Due to this structure exists isomers L-, D- and DL- lactide. Microorganisms produce L-lactide and DL-lactide is synthetic blend of D-lactide and L-lactide.

Properties of PLLA semi-crystalline polymer, which is homopolymer of L-lactide: [5,7]

- Typical melting point Tm 160-180°C
- Glass transition temperature Tg 55-65°C
- High tensile strength/modulus
- Low elongation
- Strength around 60 MPa
- Modulus around 3 MPa

2 POLYMER MODIFICATION

Polymer modification is very broad term, which includes large number of methods physical and chemical transformation of polymers. This is intentional transformation performed for the purpose of obtaining new polymer material with different properties. Due to increasing demands for properties of polymers with relation to still expanding fields of their usage importance of modification is still increasing. [1]

To obtain modified polymer is used these methods:

- Physical modification
- Mechanical-chemical modification
- Chemical modification

2.1 Physical modification

This easiest method still has wide range of usage. Physical modification with modifying substances is not incorporated into polymer chains, but stays dispersed in mass of polymers. [1]

- o Mix two or more polymers- very simple method, which often leads to excellent mechanical properties of polymer mixture
- o Using additives – additives influence physical and mechanical properties of polymer. Macromolecular substance functions as binder and defines basic physical and mechanical properties of polymers. Additives can be organic or inorganic basis.

2.2 Mechanical-chemical modification

To mechanical-chemical modification of polymers occurs by reaction of active particles, which arise at mechanical destruction of macromolecular chains. There are two basic methods: [1]

- o Mechanical degradation of polymer mixture- in the first case modified polymer is formed by combination of macroradicals, eventually by reaction macroradicals with mechanically activated polymer chains.
- o Mechanical degradation of polymer in presence of monomer- macroradicals initiates polymerization of presence monomer.

2.3 Chemical modification

By chemical modification we understand, intentional transformation of chemical structure by active chemical substances or reaction conditions. In terms of macromolecular chains length, we can divide chemical reactions of polymers to: [1]

- o Degree of polymerization remains unchanged- they are also called polymer-analog transformation this group include hydrolysis, etherification, halogenations and others.

- o Degree of polymerization is changing- increasing or decreasing size of macromolecules for example grafting, cross-linking, degradation or depolymerization.

3 ANNEALING OF POLYMERS

Heating of polymeric material below its glassy transition temperature in order to relieve the internal stresses inducted into the material during manufacturing and it is called annealing of plastics.

Plastic mold is soften by heating and then forced into a cavity where it cools down and shrinks. Non-uniform soft plastic flowing and non-uniform and relatively fast cooling result in a formation of internal stresses, which could cause dimensional distortion of the part and even cracking.

Molded parts machining introduces additional internal stresses particularly if an improperly designed tool is used of if the plastic material is locally overheated because of excessive cutting and feed speeds also deep hole drilling, uneven thickness reduction and thread screw cutting are the machining operations producing internal stresses, which should be reduced by annealing. [19]

Technology of plastics annealing

Procedure: 1.Place plastic part in annealing oven

2. Heating and holding part at annealing temperature and controlled rate.

3. Cooling part

Techniques:

- Batch annealing
- Conveyorized forced hot air annealing
- Infrared annealing

4 X-RAY DIFFRACTION

X-ray diffraction is used for determination of material properties such as identification unknown polymers, additional substance and degree of crystallinity or orientation. Structure properties are closely related to physical properties, which are strength, toughness, density and others. Most frequently used radiation for polymers is CuKα of wavelength 1,54 A. There are two basic methods for obtaining information, first method is registration of dispersed radiation photographically and it is registration by detectors of diffracted radiation and goniometers. Computer goniometric procedures give us so-called diffraction curve. This diffraction curve has each substance different so the tested material can be easily identified. There is also catalog ASTM, there are also various reflexes and intensity of different materials. [20]

By X-ray diffraction can be distinguished between arranged and disordered structures, for example crystalline substances have several diffraction spots-peaks, unlike amorphous materials, which have x-ray spectrum rather diffuse character. Each polymer has unique structure, some crystallize, others only partially, so the diffraction records have relatively sharp peaks and amorphous halo. X-ray diffraction also can be used to distinguished polymer modification. Generally x-ray diffraction performed is in range of big or small diffraction angles by technique on pass or on reflection. [20]

Degree of crystallinity

This important characteristic can be also determined from diffraction curve. Degree of crystallinity significantly affects physical properties of polymers, which are density, stiffness, hardness, flexibility, melt temperature and others.

Advantages of x-ray diffraction

- Easy method of determining material phase structure
- Only direct method of determining crystal lattice, crystallinity and orientation
- Do not require special preparation test samples
- Structure of test sample is not breached
- Requires small amount of test sample
- Short measurement time
- Possibility direct observation and quantitative data processing in computer [20]

5 HARDNESS

Hardness of materials can be determined several ways:

  o Resistance to indentation¨

  o Rebound efficiency

  o Resistance to scratching

The first method is the most commonly used technique for plastics. Numerous test methods are available for the measurement material resistance to indentation, but they differ only in detail. Basically they all use the size of an indent produced by hardened steel of diamond indenter in the material as an indication of its hardness, the smaller indent is created, the harder the material, and so the greater the hardness number. Hardness tests are simple, quick and nondestructive, which account for their wide use for quality control purposes. [2,13]

The larger the resistance to deformation, the harder the body appears. From this more everyday experience arise a definition of hardness that is used generally in technology. However, only the hardness of relatively soft materials can be assessed with fingers. The hardness testing of technically more interesting, much harder materials is possible only with testing apparatus.

Hardness H is defined as resistance to with which a body counters the penetration of foreign body. The resistance to deformation is:

$$H = \frac{F}{A} \tag{1}$$

Where F is test force and A is the indentation surface.

From the deformation of the material by the defined load is then the hardness value is calculated. Accordingly with these specifications have to be made, for the definition of hardness testing method: [14,15]

1. The defining equation of the hardness value taking under consideration the stress and the material reaction
2. The shape and material of the indenter
3. The force-time regime of the hardness testing method

Because the plastic deformation of the sample is always important, the hardness test cannot be repeated in same point.

5.1 Methods of measuring hardness

The most used methods of measuring hardness are indentation methods, consisting of pressing indenter by the defined force to the surface of tested material. Principally there exists 2 ways of measuring hardness. The first method works with the principle, in which an indenter is pressed to the material, in order to achieve plastic deformation of the material. These methods we designate as indentation methods. The second method of hardness measurement is based on principle of the elastic interaction between material surface and test object. [11]

The indentation tool shall not be subject to plastic deformation; therefore it has to achieve high hardness values, Young modulus and ultimate tensile. Very often is functional part of the indenter is the diamond. In view of the fact, that multi axis stress occurring during hardness measuring of the test sample, resulting hardness values are influenced by wide range of factors. The final hardness value depends on: [16]

- Elastic properties of the measured material, especially tensile modulus and shear modulus
- Plastic properties of the tested material, especially yield strength and strain hardening
- Magnitude of the pressing force, which indenter is pressed to the test sample

So it is obvious, that resulting value of hardness is influenced by material properties of tested sample. Hardness tests are divided into several groups. According to the used principle of testing hardness to: [16]

- o The scratch test, at low load the hard tip creates a stria on grinded material surface and according to width of the stria is subsequently determined hardness of measured material
- o The rebound test, during this test is hardness measured according to amount of rebound weight with spherically honed diamond tip, which hit tested object from certain height
- o The indentation test, hardness if determined by the size and shape of indentation caused by indenter

Another subdivision of the hardness testing is according the applied weight on the tested object and by response of the material to applied weight: [11]

- o Static -Brinell, Rockwell, Vickers- are most known hardness tests, test tool is pressed to the measured test sample by defined force

- o Dynamic – Poldi hammer, Shore scleroscope, duroscope – they are used in manufacturing process as control tests, force is applied by relatively high speed to tested object

The static hardness tests are divided according to standard ČSN ISO 14577-1 by amount of used force on indenter and depth of indentation to the three groups: [17]

- o Test of macro hardness $-2N<F<30000N$
- o Test of micro hardness $-2N>F, h>200nm$
- o Test of nanohardness $-0,1N>F, h<200nm$

Where F-maximum force and h-maximum depth of indention

Formerly was used for measuring hardness so-called classical imaging method based on examining dimensions of residual indentation. This method it is very easy and its essence lies in the contact with tested specimen, whose properties are know in advance, with tested material, whose properties that we are interested, and we do not know, such as elastic modulus and hardness. [11]

With the gradual development of thin layer technologies and demands on measuring local mechanical properties, the classical methods of measuring hardness became insufficient. The one of the main reasons for developing new indentation technique was also effort to determine mechanical properties of thin layers. From that reason was developed new indentation method DSI-Depth Sensing Indentation. [11]

5.2 Indentation hardness tests

For metals are used similar test methods as for plastics. The real difference is that because plastics are viscoelastic, so for the creep must be made allowance and the time-dependent recovery, which occur as a result of the applied indentation load. In this case, by the amount of permanent deformation is evaluated by hardness or material plastic flow. Flow amount may be determined by measuring the depth of the indentation or by measuring the area. Indentation depth becomes greater if the test material becomes softer. Likewise, as the test material becomes softer the projected area increases. [13,18]

5.2.1 Knoop hardness test

Knoop indenter was developed especially for indentation test with low loads, to measure micro hardness of thin metal sheets or fragile materials. [24]
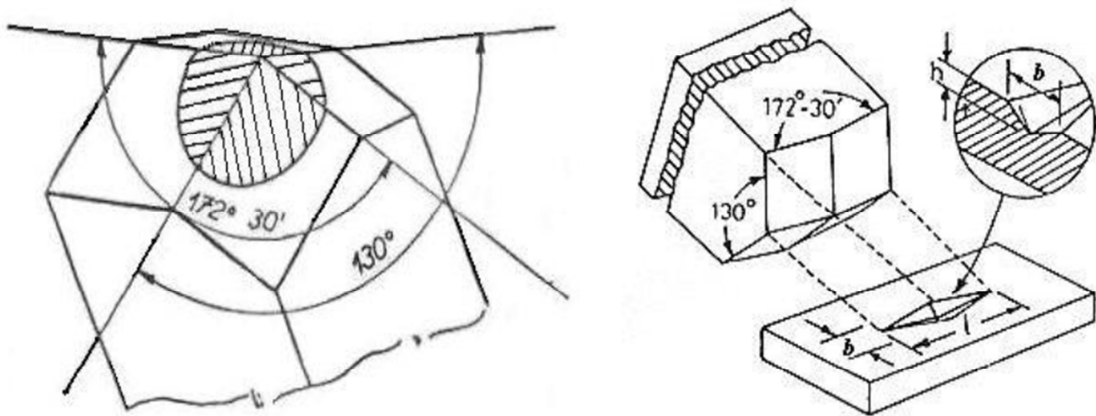
Test principle

Fig.10 Test principle –Knoop method [26]

Knoop indenter has shape of tetrahedral diamond pyramid; its indentations have shape of rhomboid. Opposite edges form and angel of 175,5° and 130°. Ratio of distances main and side diagonal is 1:7,11 and ratio of distance main diagonal to indentation depth is 30:1.

Knoop hardness is then expressed by the ratio of test load to indentation area, but it is considered as pyramid with rhomboid base and apex angles equal to angles of indented object. [25]

$$HK = \frac{p}{Cp \times L^2} \qquad (2)$$

Where L is length is indentation along its long axis, Cp is correction factor related to the shape of the indenter, P is load

Test object

Advantage of the Knoop indenter is usage for hardness determination especially hard and fragile materials, because unlike Vickers indenter is the length of main diagonal easily measurable. [25]

The tested specimen must have smooth and flat surface, without lubricants and unfamiliar objects. Test object is prepared as metallographic sample; it means that it shall not be de-

formation or thermal influence of the surface. The usual preparation is made by wet grinding and electro polishing. [23]

Test procedure

The test object must be located on stiff pad, and fixed in place. Indenter is pressed to test object by test load in perpendicular direction. Time period from the start of applying force till its final value cannot exceed 10 s. Approach speed of indenter have to be in range from 15μm/s to 70μm/s. Time period of full test load have to be in range from 10 to 15s. [23]

5.2.2 Shore

This method of the measuring hardness is based on indentation apex of the hardness tester type A, which is used for softer materials and hardness tester type D, which is used for harder materials. Method allowed hardness measurement in the beginning of indentation apex or after specified time or both. It is used only if it is not suitable scale R of the Rockwell method. [27]

Test principle

Test principle consists of the measurement specified apex depth indented in tested material under specified conditions. Depth of the indented apex is inversely proportional to value of the hardness. [27]

Test equipment

For hardness measurement is used hardness tester of the type A or type D. Hardness testers consist of the footpad, test apex, indicator of the length and calibrated spring. In footpad is opening of the diameter 3mm± 0,5 mm. Test apex diameter is 1,25 mm ± 0,15 mm made of the hardened steel located in the opening. [27]
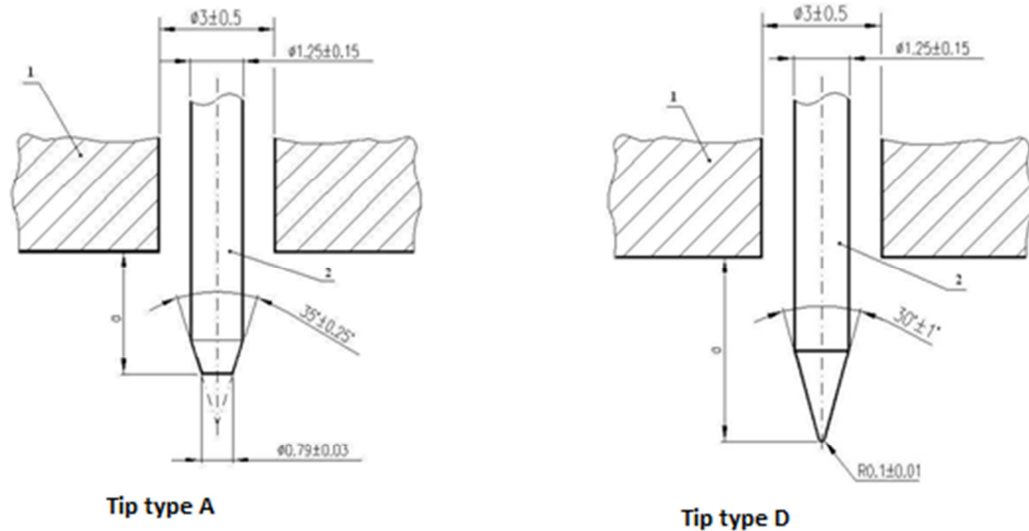
Tip type A   **Tip type D**

Fig.11 Hardness tester tips [27]

Indicator of the length serves for the reading of the test apex ejection from the footpad. I can be equipped with scale, allowing ejection reading directly in units from 0, when it is fully ejected to 100, when it is not ejected.

Calibrated springs are applied, on test apex of the hardness tester, by defined force according to the equations 16 and 17.

$$F = 550 + 75\ H_A \tag{3}$$

Where F is indentation force [mN] and H_A value of the hardness is measured by hardness tester type A

$$F = 455\ H_D \tag{4}$$

Where F is indentation force [mN] and H_D value of the hardness is measured by hardness tester type D. [27]

Test objects

Minimal thickness of the test object has to be 4 mm. If we do not have object of such thickness we can put together more of thin test object layers to reach required thickness. The results of more layered test objects do not have to match the results of one piece test objects, because with more layered test surfaces we cannot achieve perfect contact between the surfaces. Specimen surface has to be flat on a sufficiently large area, so the footpad of the hardness tester touched specimen on area of the diameter at least 6 mm from test apex tip. Hardness measurement cannot be performed on specimen with rough or curved surface. [27]

Test procedure

Test object is located on hard flat horizontal surface. Hardness tester is perpendicularly attached to specimen so the test apex tip should be located from any edge at least 9 mm. To test object is pressed, as soon as possible and without shock, the footpad. Pressure is selected according to achieve firm contact between test object and footpad.

Hardness is read on scale device after specific time. If it is required initial value of thehardness, so we read value of the hardness within one second after firm contact between test object and footpad is achieved. If hardness tester has indicator of the maximum value, so the maximum is read.

On five different places of the test object distant at least 6 mm are performed measurements and from measurements is calculated arithmetic average. [15,27]

Related standards

CSN EN ISO 868. Plastics and ebonite - Determination of indentation hardness by means of thedurometer (Shore hardness).

5.2.3 Berkovich hardness test

Formerly known as, the Khrushchev and Berkovich micro hardness test. Berkovich indenter is used for micro hardness test and nanoindentation test.

Procedure and principle is the same like Vickers micro hardness. Only change is the shape of the indenter. Berkovich indenter is tetrahedron diamond pyramid. Advantage is the walls of the indenter come together in one point unlike Vickers and Knoop four-sided indenter. Radius of new Berkovich indenter peak has size of 50 až 100 nm, with the wear the radius increasing up to 200nm. But thanks to complicated manufacturing of the four-sided pyramid indenters, it is allowed creation of common edge. Berkovich indenter is also more resistant to careless handling and impacts. [24]

Microhardness value for Berkovich indenter with angle of 65, 03°, is expressed by the ratio of magnitude of the load and area:

$$H_{CH} = 1570 \times \frac{W}{l^2} \qquad (5)$$

Where W is magnitude of the load [kg] and l is measured height of triangle in indentation. Ch comes from earlier name of Berkovich test known as Khrushchev and Berkovich microhardness test. [25]
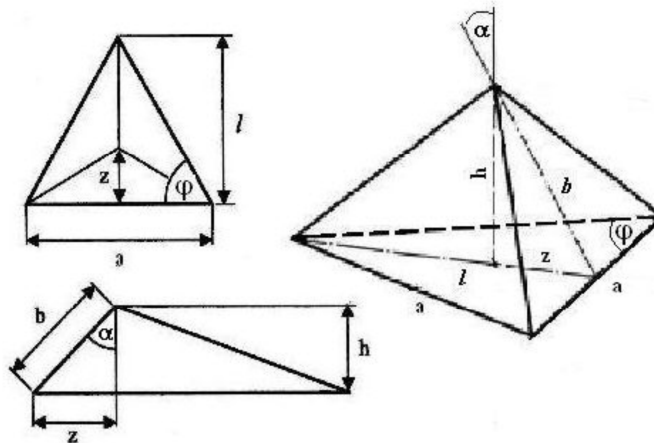

Fig.12 Indenter shape-berkovich [25]

6 DEPTH SENSING INDENTATION –DSI

Earlier was used for measuring hardness so called classic display method based on measuring dimensions of residual indentation. With development, technology of measurement thin layers and demands of measuring local mechanical properties became insufficient. Their main disadvantage lies especially in impossibility of measurement very thin layers and highly elastic layers. That's the main reasons for development new indentation technique called DSI – depth sensing indentation. [11]

Depth sensing indentation has origins in seventies of 20 century (Bulychev and Alekin). Substantial improvement of methodology, analysis and gathering data have made Oliver and Pharr, in the beginning of 80s. [25]

To enhance the information gained from measurements hardness on plastic, it is necessary to record both force required by the indenter to penetrate the test sample and the indentation depth over the entire indenting process. For this purpose is process of the indentation recorded and information on the viscoelastic –plastic behavior of the polymer is derived by the evaluation of loading and unloading curves. The DSI method can be performed either load or indentation depth controlled, or at a constant indentation strain rate. Various indenters are used: rectangular based Vickers or Knoop pyramids, triangular-based Berkovich pyramids or so called "cube corners", conical tips or even specially rounded indenters. [22]

With instrumented indentation test can be measured hardness values, indentation modulus, strain hardening exponents and viscoelastic properties. Fracture toughness of brittle materials also the influence of residual stress in solid material or thin layers, or the elastic behavior of miniaturized components are also measurable. The presence of orientations can also be detected. [22]
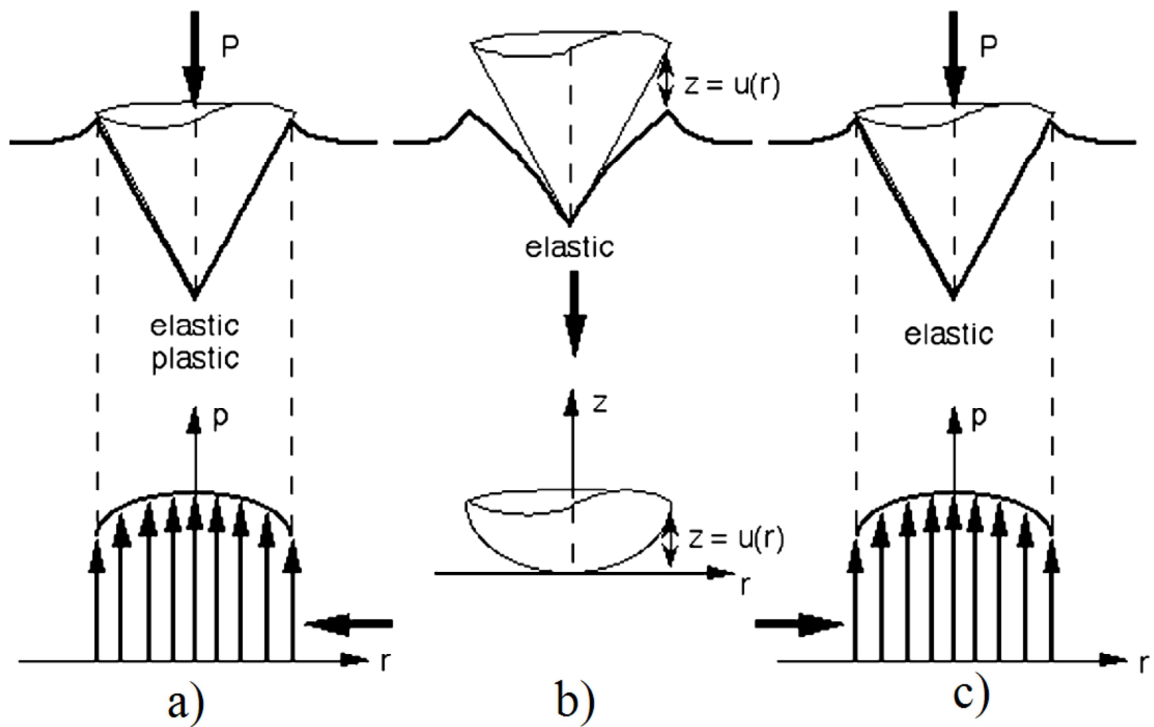
Fig.13 Concepts used to understand and define the effective indenter shape [12]

The following functional dependencies can be measured:

- Load as a function of indentation depth during load increase
- Load and indentation depth as functions of time for determining relaxation and creep behavior
- Elastic recovery during reloading

This enables, during hardness measurement, the separation of the plastic and elastic components of total deformation. [22]

6.1 Determination of parameters

In fig.14 is presented schematic representation of a typical data set obtained with Berkovich indenter, results of depth sensing indentation are immediate values of parameters P designates the load and h the displacement relative to the initial undeformed surface. [25,28]

Deformation during loading is assumed to be both elastic and plastic in nature as the permanent hardness impression forms, for the purpose of modeling. It is assumed that only the elastic displacements are recovered, during unloading, the unloading curve elastic nature that facilitates the analysis. [28]
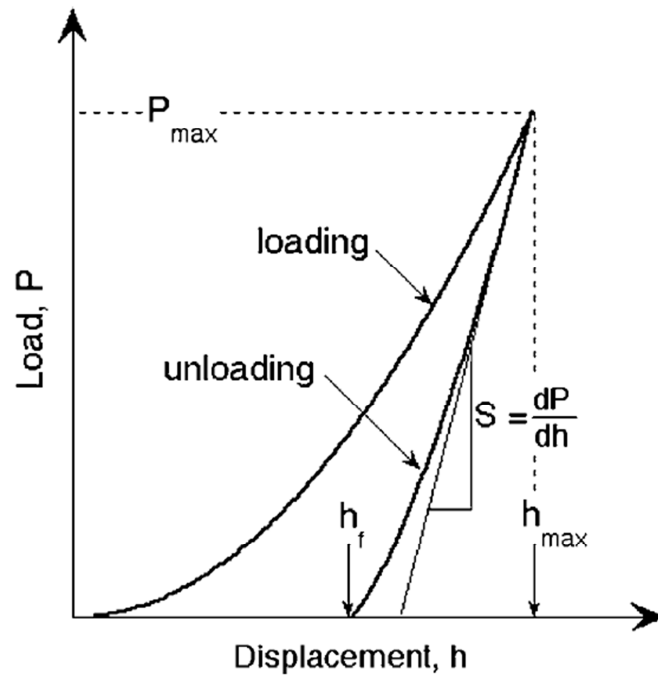
Fig.14 Schematic illustration of indentation load-

Displacement data showing important parameters [28]

Basic measured quantities are maximum loading force P_{max} maximum indentation depth h_{max} and elastic unloading stiffness S that can be defined as the slope of the upper portion of the unloading curve during initial stages of unloading and it is also called the contact stiffness. [28]

Contact stiffness S is calculated from following formula:

$$S = \left(\frac{dP}{dh}\right)_m \tag{6}$$

Course of loading force P:

$$P = P_{max} \cdot \left(\frac{h - h_p}{h_{max} - h_p}\right)^m \tag{7}$$

Depth h_c is calculated by the depth of indenter contact with test sample during P_{max} and h_r is depth intersection of the tangent to the axis. [11]

$$h_c = h_{max} - \varepsilon \cdot (h_{max} - h_r) \tag{8}$$
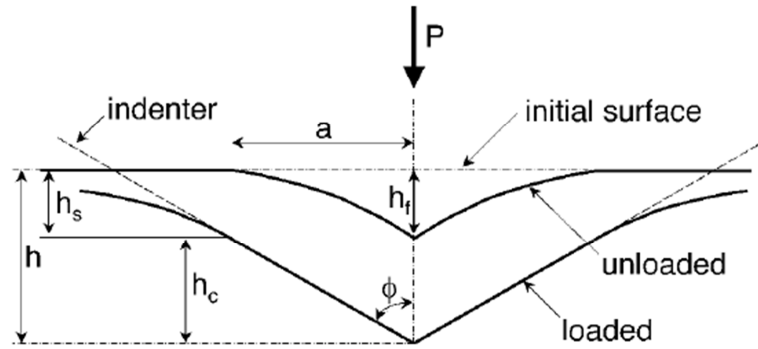
$$h_r = h_{max} - \frac{P_{max}}{S} \tag{9}$$

Fig.15 Schematic of unloading process [12]

6.1.1   Hardness

Indentation hardness H_{IT} is a measure of resistant to permanent deformation or damage.

The indentation hardness H_{IT} is generally defined as maximum loading force P_{max} and projected (cross-sectional) area of contact between the indenter and specimen determined from the load indentation depth curve and the area function of the indenter in mm^2 A_p. [11]

$$H_{IT} = \frac{P_{max}}{A_p} \tag{10}$$

The first approximation to the projected area A_p, for the indentation depths h>6 μm, is given by the theoretical shape of indenter. [11]

For standard Vickers indenter that is:

$$A_p = 24,50 \cdot h_c^2 \tag{11}$$

For standard Berkovich indenter that is:

$$A_p = 23,96 \cdot h_c^2 \tag{12}$$

The *Martens hardness* is measured under applied test load F and contains the plastic and elastic deformation energy of indentation, so it can be used for all materials. It is determined from curve load/depth of indentation in increasing test load area.

Martens hardness HM is defined as the quotient of test load P and the contact area calculated from the corresponding indentation depth h:[11]

$$HM = \frac{P}{A_s(h)} \tag{13}$$

For standard Vickers indenter is surface area A_s :

$$A_S(h) = \frac{4 \cdot \sin\left(\frac{\alpha}{2}\right)}{cos^2\left(\frac{\alpha}{2}\right)} \cdot h^2 \qquad (14)$$

For standard Berkovich indenter is surface area A_s:[11]

$$A_S(h) = \frac{3 \cdot \sqrt{3} \cdot tan\alpha}{cos\alpha} \cdot h^2 \qquad (15)$$

6.1.2 Elastic modulus

Another material parameter that we can obtain from the indentation tests by DSI method is indentation modulus E_{IT}, reduced modulus E_r and complex modulus E^*.

In the ideal case indentation modulus has equal importance as elastic Young modulus. Generally is indentation modulus determined from slope of the tangent used to calculate indentation hardness H_{IT}, while for indentation modulus is applied: [11,25]

$$E_{IT} = E^* \cdot (1 - v_s^2) \qquad (16)$$

Where v_s is Poisson ratio of test sample, for metal materials from 0,2 to 0,4 and for polymer materials from 0,3 to 0,4 and E^* is complex modulus.

Reduced modulus E_r is defined from the following equation: [11,25]

$$E_r = \frac{\sqrt{\pi}}{2 \cdot C\sqrt{A_p}} \qquad (17)$$

Where A_p is projected contact area, value of the indenter area function at contact depth and C is contact pliability.

Complex modulus E^* is defined as: [11,25]

$$E^* = \frac{1}{\frac{1}{E_r} - \frac{1-v_i^2}{E_i}} \qquad (18)$$

Where E_i is modulus of the indented tool, E_r is reduced modulus of the indentation contact and v_i is Poisson ration of the indented tool.

6.1.3 Indentation creep

If during constant load is measured change of indentation depth, than we can calculate relative indentation depth, it is value of the indentation creep.

Indentation creep C_{IT} is defined from equation:

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \qquad (19)$$

Where h_1 is indentation depth in time T_1, when test load is achieved and h_2 is indentation depth in time T_2, during endurance to achieve maximum test load. [11,17]
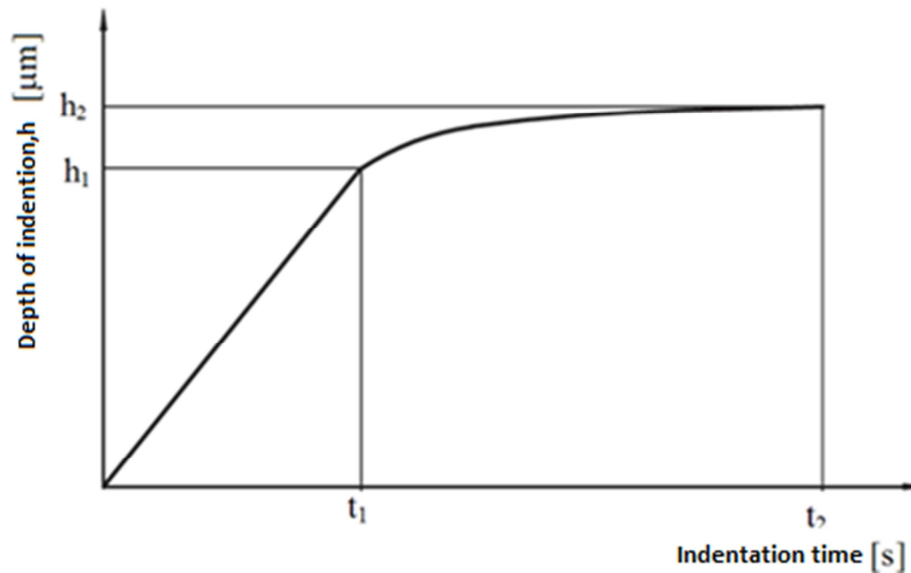

Fig.16 Indentation creep [11]

6.1.4 Indentation relaxation

If during constant depth of indentation is measured change of test loading than we can calculate relative change of test loading, or value of relaxation R_{IT}: [11,17]

$$R_{IT} = \frac{P_1 - P_2}{P_1} \cdot 100 \qquad (20)$$

Where P1 is load after achieved depth of indentation, which is maintain on constant level and P2 is load after time, when was depth of indentation maintained on constant level.
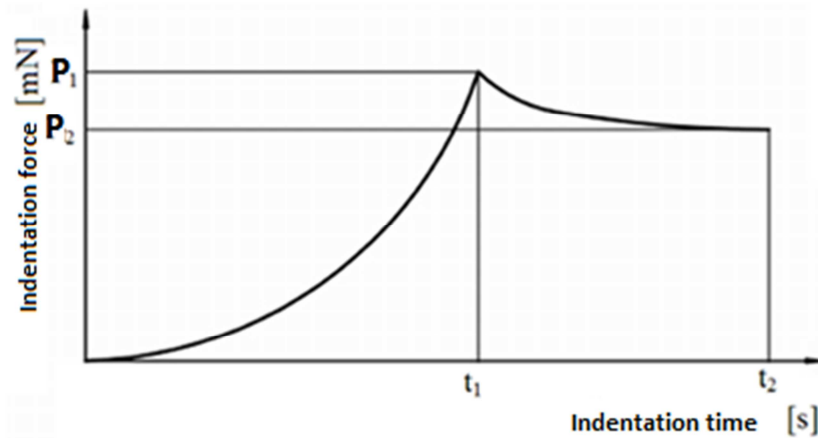
Fig.17 Indentation relaxation [11]

6.1.5 Deformation work

Indentation curve is generally source of big amount of information. Total work W_{total} consumed in indentation cycle process is equal to area under loading curve. Area between loading and unloading curve indicates irreversible plastic work W_{plast} and area under unloading curve is elastic work W_{elast}. Coefficient of reverse relaxation η_{IT} is defined as quotient of elastic work W_{elast} and total work W_{total}. [11,17]

$$W_{total} = W_{plast} + W_{elast} \tag{21}$$

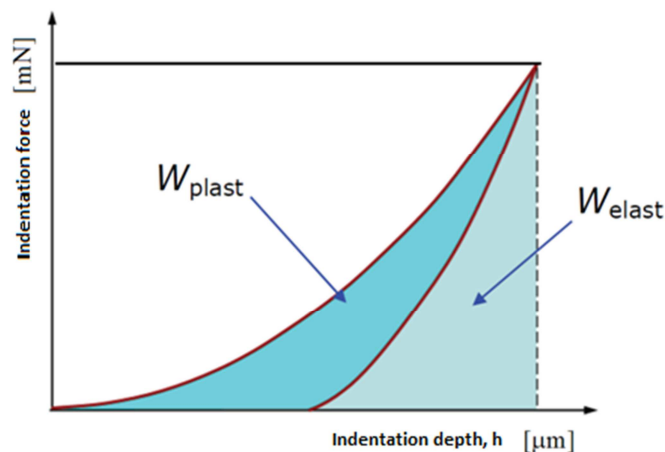$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \tag{22}$$

Fig.18 Deformation work [11]

6.2 Data processing methods

Basic of the mathematical analysis measured indentation data is Herz equations, the premise is only the existence of ideal elastic contact. During indentation of the ideal plastic behavior has loading part of the indentation curve also parabolic process and unloading part is parallel to vertical axis. For now still not exist theory that could exactly describe case of indentation to elastic-plastic material. Analytical solution leads to complicated nonlinear equations with many parameters describing material behavior. [25]

The first concept of method, specified for extraction of hardness and elastic modulus from indentation data, created Doerner and Nix. They expected that if change of the contact surface is small, so the indenter assume as cylinder during unloading phase. [10,12]

Oliver and Pharr later came; based on many indentation experiments with different materials, with conclusion that premise of line during unloading phase is not exactly correct. They suggested approximating unloading curves by power function. [28]

6.2.1 Doerner and Nix method

Inventers of this method are Doerner and Nix, which during indentation experiments with Berkovich indenter watched liner character of unloading curves early phases within wide group of materials. In analysis they replaced Berkovich indenter with conical and proceeded from equations for flat punch. Method is based on premise that in early phases of unloading, contact circle radius stays constant. Tip of indenter is still in same contact with deformed surface; indentation depth is decreasing due to elastic regeneration of surface. It means that early phase of unloading is linear i.e. is similar to flat punch. [10]
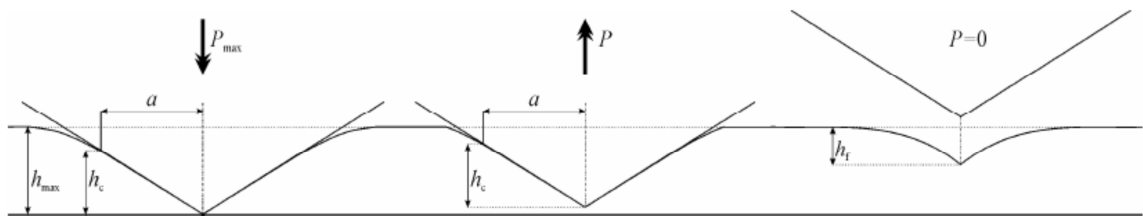

Fig.19 Schematic of indentation depth [10]

Essential is in this case limit depth h_c, during which is contact circle radius constant. Its calculation is based on linear extrapolation of early unloading phase, unloading curve to zero loading force. Intersection with horizontal axis of displacement represents h_c. When is

determined contact depth h_c, it is possible used known geometry of the indenter tip and calculate projection of contact surface and then modulus with hardness. [10,11]

The initial sections, approximately one third, measured unloading curves were approximately linear. Because of that, equations based originally for cylinder indenter were used for start of unloading, on premise that contact area in this section is constant. Extrapolation of initial section was determined depth of indentation plastic part size which was substituted to equation for hardness calculation.

$$H = \frac{P}{A_c} = \frac{c \cdot P}{h_c^2} \tag{23}$$

Where P is loading force, c is geometric constant and h_c is depth of indentation. Problem of this method is that the results depend on how many points of unloading curve initial section is included in calculation. This method is used and it is considered compliant especially within materials with bigger plastic deformation part. [10]

6.2.2 Oliver and Pharr method-multipoint

Method is based on premise elastic-plastic loading and elastic unloading. Basic measured valuables determined in analysis are maximum loading force P_{max}, maximum indentation depth h_{max} and contact stiffness S, defined as slope of the tangent initial part of unloading curve. Method is based on Doerner and Nix procedure, unloading phase is not expected linear, but it is approximated by power function. [11,12,28]
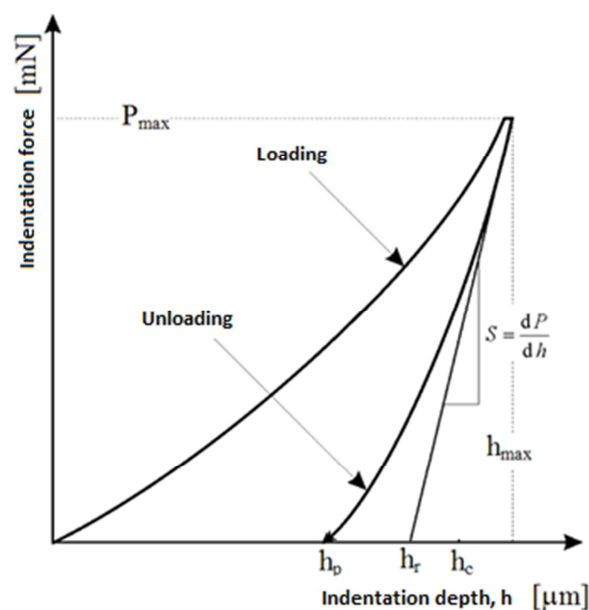

Fig.20 Indentation curve [12]

Principle of multipoint method consist in determination of tangent slope, led to beginning of unloading curve, while intersection of tangent with axis s determining contact depth h_p. By equation derivation we determine slope of tangent: [12,28]

$$\frac{dP}{dh} = 2 \cdot \frac{2 \cdot E^* tg\alpha}{\pi} \cdot h_e \tag{24}$$

Where loading force P is:

$$P = \frac{1}{2} \cdot \frac{dP}{dh} \cdot h_e \tag{25}$$

Equation for depth h_a is:

$$h_a = \left[\frac{2 \cdot (\pi - 2)}{\pi}\right] \cdot \frac{P_{max}}{dp/dh_{max}} \tag{26}$$

If we replace square bracket by symbol ε, then we can determine contact depth h_c as: [11,12]

$$h_c = h_{max} - \varepsilon \cdot \frac{P_{max}}{dP/dh} = h_{max} - \varepsilon \cdot (h_{max} - h_f) \tag{27}$$

Where ε is constant which depends on geometry of indenter. Values that are important: ε=0,72 for conical punch (indenter), ε=0,75 for spherical indenter, Vickers and Berkovich and ε=1 for flat punch. If the shape function of the tip is known A_p=f (h_c), than hardness H can be determined from equation:[12]

$$H = \frac{P_{max}}{A_p \cdot (h_c)} \tag{28}$$

Complex elastic modulus is calculated:

$$E^* = \frac{dP}{dh} \cdot \frac{1}{2 \cdot a} = \frac{1}{2} \cdot \frac{dP}{dh} \cdot \frac{\sqrt{\pi}}{\sqrt{A}} \tag{29}$$

The real geometry of Berkovich indenter was not considered. It is needed to use geometric correction factor β= 1,034, which contain pyramidal deviation from axial symmetric indenter, for which was equation originally derived: [28]

$$\frac{dP}{dh} = \frac{1}{\beta} \cdot \frac{dP}{dh} \tag{30}$$

6.3 Indentation curves

Method DSI is used for wide range of materials, from soft polymer to hard carbon diamond-like layers. Depth sensing indentation method is based on continual process loading force P and immediate location of indenter h. Graphic expression of this relationship is indentation curve. [11]

On other words, the response of measured material by indentation is main factor, which influence the shape of indentation curve. Shape of indentation curve is not only for calculation of hardness and elastic modulus, but is also source of very important information, which is showed by random discontinuous course for example phase transformation, cracks and layer delamination. [25]
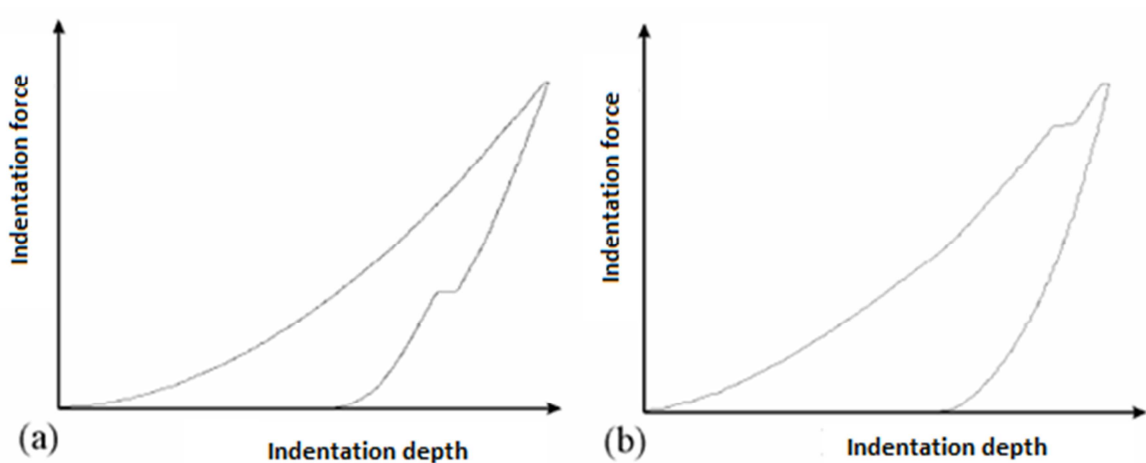
Fig.21 Discontinuous process of indentation curves (a) Phase transformation, (b) Crackling after transformation [11]

As supplementary information about response of material to loading/unloading we can use graphic dependence-time or dependence depth of indentation-time. [11]
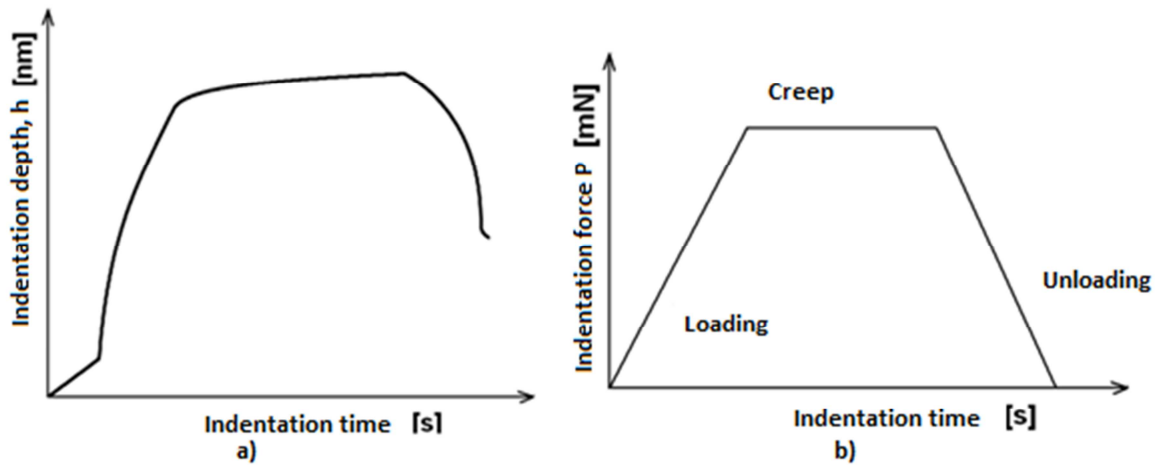
Fig.22 Relations a) load- time b) indentation depth – time [11]

Due to the fact that indentation tests initiate in material tri-axial stress state, it is showed difference between graphical progresses of tensile tests namely uniaxial stress state and tri-axial stress state deduced by depth sensing indentation. [11,25]

According to reaction of outer applied force materials can be divided to three groups: [11]
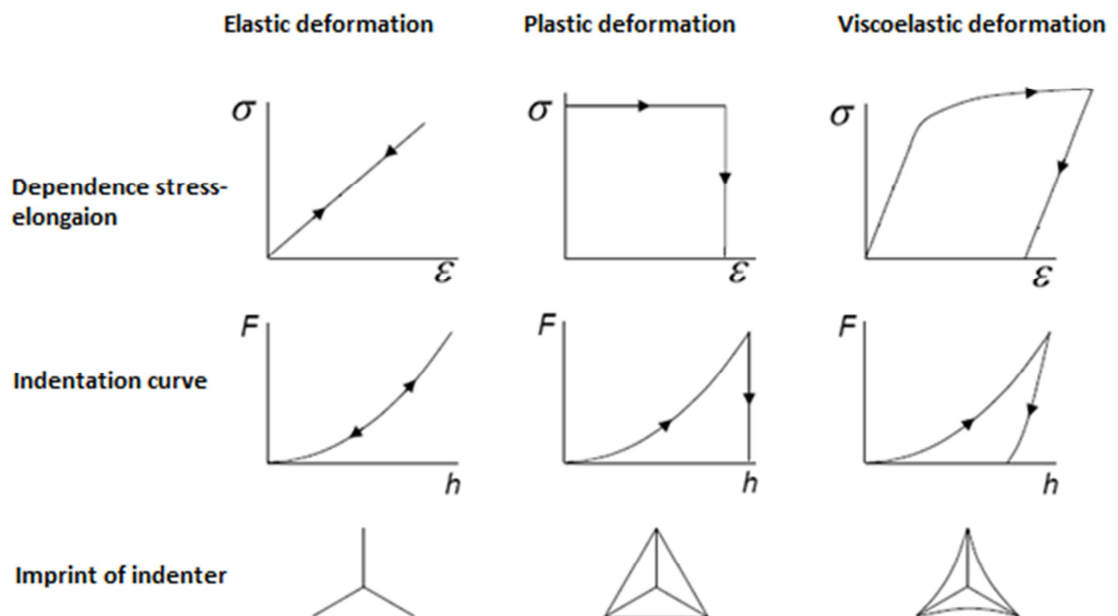
- Elastic
- Plastic
- Elastic-plastic (viscoelastic)

Fig.23. Characteristic shapes of indentation curves for different materials [11,26]

It should be noted that for now still do not exist theory, which is exactly describing process of indentation to elastic-plastic material. Analytical solutions led to complicated non-linear equations with lot of parameters, describing behavior of material by using finite elements methods. [11]

6.4 Factors influencing test accuracy

Unlike common hardness tests is depth sensing indentation method based on indirect determination hardness values from precise determination depth of indentation to test sample. In practice is very difficult to precisely measure indentation depth and loading force so the results are influenced by errors. [11]

Factors influencing precise measurement can be divided to two groups: [11]

- Influence of measure device properties:
  - Temperature fluctuation
  - Determination of indenter first contact point
  - Measuring device stiffness
  - Indenter geometry

- Surface properties of measured material:
  - Shape of indentation (pile-up, sink-in)
  - Indentation size effect
  - Sample surface quality
  - Residual stress
  - Influence of the substrate

6.4.1 Temperature fluctuation

Two types of the temperature fluctuations generally occur during indentation tests. First of them is result of the plastic flow inside measured sample namely creep. Creep is observed during constant loading force, when growth of indentation depth occurs, because indenter tip penetrates deeper into material sample. Another reason of indentation depth change is device dimension change due to temperature fluctuation, which is unfortunately unrecognizable from material creep. If is measured change rate if depth with time during constant loading in any moment of depth sensing indentation test then it is possible to calculate temperature fluctuation and on basis of its size regulate recording of depth during depth sensing indentation test.[11,25]

Detailed study of the temperature fluctuation performed in work Feng and Zhang. They discovered that increase of temperature inside material can be considerable, but material volumes during micro and nanoindentation tests are too small, that any change of dimension test sample is lower than 0,1 % from total indentation depth, which is negligible. We have to realize that local increased temperatures inside test sample can influence for example viscosity and hardness of measured material. For calculation temperature fluctuation level is generally advised used data gained in the end of unloading phase, because here during low loading there is small probability that inside test sample occur creep. Vice versa for determination of test sample creep behavior is loading maximal. Temperature fluctuation speed is determined by linear regression from measured indentation characteristic loading/depth during constant loading force. [11]

6.4.2   Determination of indenter first contact point

Key for right measuring indentation depth therefore evaluation of the hardness and other properties is determination of neutral indenter position. The Ideal situation would occur if the indenter tip is touching the surface of measured material. It will be created the initial contact of indenter tip and surface of measured test sample without deformation influenced surface of test sample. But in practice the neutral position of test sample is determined so that indenter tip penetrates to material surface during lowest possible loading, which measuring device can develop. Minimal indentation depth is then marked as initial and following measured depth is influenced by initial depth. [11,25]

6.4.3   Measuring device pliancy

Pliancy of measuring device is influencing to the certain extent hardness measurement. The usage of higher device pliancy values than actually, leads to reduction measured values of indentation depth and measured pliancy of test sample, so the determined values of elastic modulus and hardness are higher than actually. If the elastic modulus is constant, pliancy of specimen is decreasing with increasing indentation depth, thus even loading, which contributing to the growth of measured values. Error is greater at higher loading force values and test sample with higher elastic modulus and lower hardness. Pliancy is defined as quotient of device dimension change and corresponding change of loading force size. [11]

6.4.4   Indenter geometry

Due to the fact that key value for hardness determination by depth sensing indentation is projection area, designated from indenter depth penetration to test sample, shape of indenter is very important factor. All analysis assumes ideal shape of indenter tip, which is in practice often unachievable. To deviation from ideal shape of indenter contributes wear and tear, in case diamond indenter also anisotropy of crystal. Exact geometry knowledge of indenter tip is one important factors influencing results of indentation measurement.

To determine real projection area at the indentation depth it should be considered correction factor, which shows degree of deviation from ideal value. Assuming that real area is A and ideal area is A_i then is correction factor expressed as: [11]

$$A = \pi \cdot \left[\frac{dP}{dh} \cdot \frac{1}{2E^*} \right]^2 \qquad (31)$$

Ratio A/Ai is usually plotted depending on the depth. If the value of ratio is bigger than one, it means indenter tip is worn and result is then higher value of hardness and vica versa. [25]

6.4.5   Indentation shape

Main goal of indentation tests is microhardness determination and simultaneously elastic modulus of test sample, deformation work, creep, recording values of process applied loading on indenter and indentation penetration depth. If the test sample is plastically deformed, leaves in surface permanent indentation. Size of created indentation during depth sensing indentation test is too small for precise measurement by optical techniques, like conventional hardness tests. During unloading occurs so-called size indentation relaxation i.e. material tries to return to its original shape by effect of elastic deformation. [11,25]

Initial deformations emerging during loading indenter tip are usually elastic. With gradual increase of loading force leads to increase pressure under indenter. If this induced stress exceeds yield strength then manifest significant plastic deformation.

There are two basic types of deformation around indentation. If during indentation process occur only elastic contact then the material is pulled around indentation and it is called sink-in effect. But in practical work occurs elastic-plastic contact a then it can happen either pulling material around indentation i.e. sink-in effect or accumulation of the material

around indentation i.e. pile-up effect. It is necessary to be noted that analysis according Oliver and Pharr assumes clean elastic-plastic contact with occurring sink-in effect. [11]
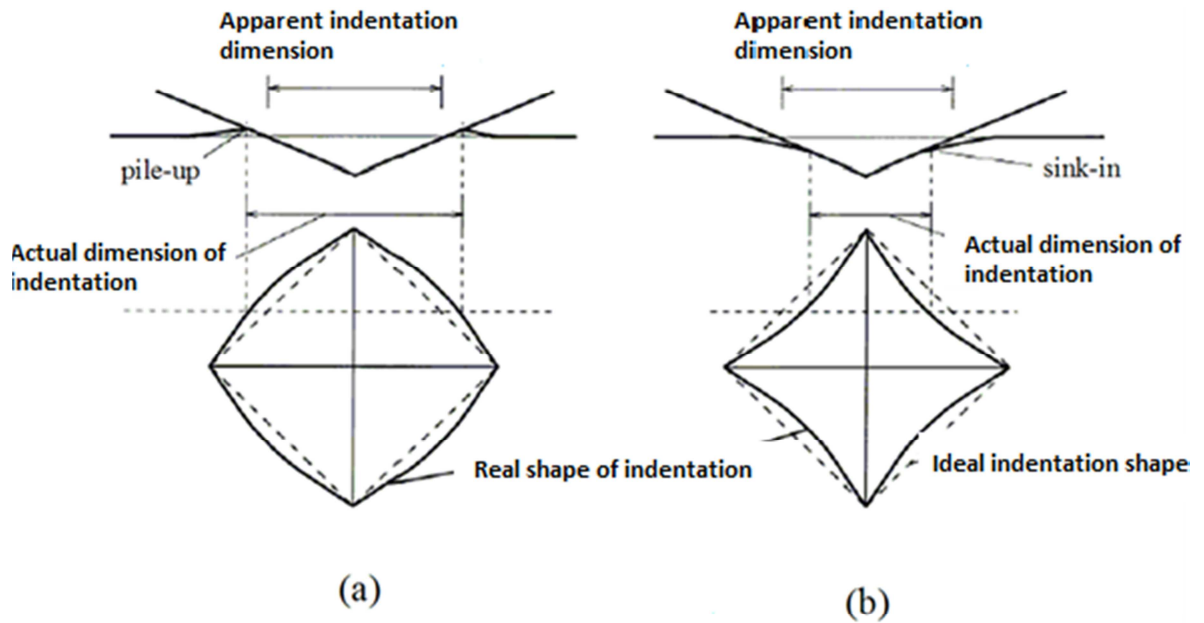

Fig.24 Indentation shape a) pile-up b) sink-in [11]

Whether in case elastic-plastic or plastic deformation occurs, sink-in or pile-up effect can be described based on ration E/Y, where E is Young modulus and Y is yield strength. Generally valid is that if the ratio for specific material E/Y is big, then during indentation effect pile-up will dominate. Vice versa if the ration is small, effect sink-in manifest at indentation. [11]
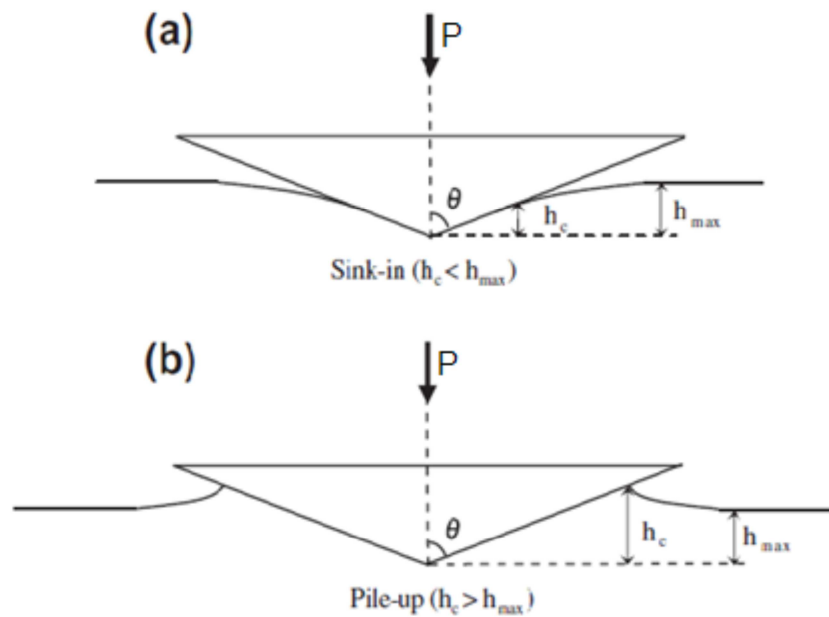
Fig.25 Schematic a) sink-in b) pile-up [11]

6.4.6 Indentation Size Effect -ISE

This effect significantly manifest during micro and nanohardness test at loading lower than 5N, when with decreasing loading occurs increase in hardness. For indenters, which are geometrically similar to Vickers pyramid applies that hardness must be independent on applied loading. The most common causes of ISE that can be found in literature: [11,25]

- In the moment, when is lowered loading force, begin to significantly show shake and vibration of measuring device and consequence is increase of indentation size a so reduced hardness

- Increase in hardness is consequence of mechanical polishing test sample surface, when exact material layer is solidified by deformation

- During common measurement of indentation size from indentation picture is usual resolution of the optical microscope $\pm$ 0, 5 μm and therefore is accuracy at lower loading forces worse due to difficulty of measured indentations

Due to definition of hardness H=P/A we can found in literature many models, which are trying explain ISE using improperly deducted indentation size or indentation force process i.e. response of material to indentation. Farges and Degout in their work created empiric model explaining ISE based on accumulation of material around indentation, so pile-up effect and therefore wrongly deducted diagonal of indentation. For Vickers indenter is in-

troduced so-called Vickers correction distance L_v and measured value of hardness expressed as: [11]

$$H^* = H_0 + \frac{2 \cdot L_v \cdot H_o}{d^*} \qquad (32)$$

Where d^* is measured diagonal of indentation, H_0 is so-called absolute hardness i.e. macrohardness independent on loading force.

6.4.7 Measure sample surface quality

It generally known that many useful material properties depending on their surface properties, there are mainly technological properties such as friction or abrasion. A technological characteristic often decides about reliability and durability of individual parts. Another indispensable group is chemical properties of surfaces, which is most important material resistance against corrosion. [25]

It is obvious that surface of any material is never perfectly flat. On macroscopic level, surface quality has insignificant influence on depth indentation sensing, because the size and depth of indentation reaches far beyond surface roughness. However at macro and nanoindentation test is already surface quality important factor. Character of surface quality brings errors into determination of contact area between indenter and test sample. Generally contact is not between two objects controlled by just material properties but also topographic properties. [11]

Consequence of surface roughness is irregular contact between indenter and test sample. Local stress is increased by irregular contact; material is deformed into greater depths at relatively low loading. Result is in case of low quality lower value of hardness compared to higher surface quality of same test sample. When using spherical indenters, surface quality has greater influence final size hardness value than usage of conical indenters. [25]

6.4.8 Residual stress

Basic characteristics of surface layer are determined by manufacturing conditions. Last manufacturing process has not just decisive influence on exact surface or surface layer but also on whole component. Residual stresses are defined as stresses which are located in material without effect of outer loading. Surface residual stresses can be beneficial but also harmful. Generally is elongation stress considered as harmful and undesirable. On the con-

trary pressure stresses improve fatigue properties of material and limiting creation and spreading of surface cracks.

Main causes of residual stresses are: [11,25]

- Uneven plastic deformation in machined surface of material
- Uneven heating and cooling material, which causes its expansion and contraction
- Uneven structure changes, caused by heat and mechanical forces
- Chemical processes connected to particle reaction penetrating to surface layer

In case of indentation methods exists direct link between hardness change and stress, if stress values are in Hook law range. Generally is valid that tensile stresses cause significant hardness change than pressure stresses. [11,25]
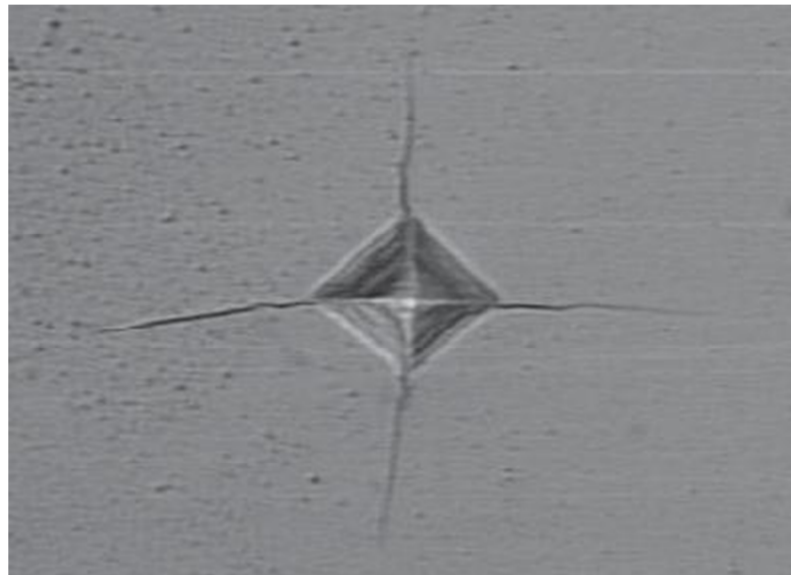
Fig.26 Surface crack [11]

6.4.9 Substrate influence

One of the most common applications for micro-indentation and nanoindentation tests is measurement of mechanical properties of thin layers. Standard methods are evaluation of indentation data however they were developed mostly for monolithic materials. It is necessary to realize some limitation and adapt to them experimental parameters, so they can be used for thin layers. Until now was considered only very thin layer, but in practice this refers to system of thin layer-substrate. [11]

In material research, we are mostly interested in mechanical properties of thin layer but not whole system layer-substrate. Basically exist two ways how measure only properties of thin layer. First possibility is to first perform measurement and then from combined response of layer-substrate extract layer and substrate properties. Second option allows perform measurement, so the influence of substrate is insignificant. [11]

II. EXPERIMENTAL PART

7 AIMS OF THE MASTER THESIS

Aim of this master thesis is research of micromechanical properties modifies PLA. DSI – Depth sensing indentation method was used for PLA micromechanical properties measurement to compare unmodified and modified micro-mechanical properties changes of chosen PLA.

Procedure to solve master thesis:

- o Commissioned study on the given topic
- o Preparation test samples for experimental part
- o Performing experiment
- o Evaluation of the measured results

8 CHOSEN MATERIAL– PLA

Test sample material is from company NatureWorks LLC. Manufacture name of material is Ingeo Biopolymer 4043D. General purpose is biaxially oriented films.[29]

Properties of this material from manufacturer:

Table 1 Properties of PLA [29]

Density		1,24 g/cc
Tensile Strength		124 MPa
Tensile Modulus		3585 MPa
Elongation at Break		130%
Optical characteristics	Haze	2,1%
	Gloss 20°	90
Thermal characteristics	Melting point	145-160°C

9 PREPARATION OF TEST SAMPLES

9.1 Injection molding

Polymer material test samples for microhardness tests were manufactured by injection molding technology on injection molding machine. Shape of test samples was manufactured according standard CSN EN ISO 527-1 and dimensions were reduced. Injection molding parameters were set as recommended by the material manufacturer.

Fig.27Arburg AllROUNDER 470 C
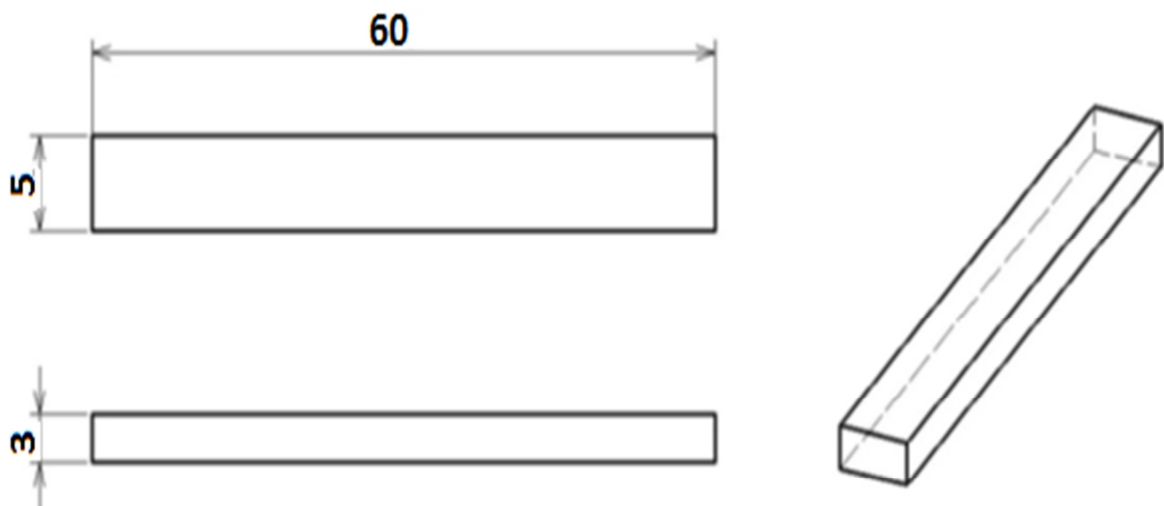
Fig.28 Dimensions of test sample

9.1.1 Setting of injection molding machine

Table 2 Processing temperature profile

Melt temperature	210± 8°C
Feed throat	45°C
Feed temperature	180°C
Compression section	190°C
Metering section	200°C
Adapter	200°C
Die	200°C
Screw speed	20-100rpm
Heat set oven	120-140°C

9.2 Annealing

Annealing was made in oven Mora VT 4807.

Annealing settings was 1 hour for each temperature 90, 100, 110, 120, 130, 140 ^{0}C.

Fig.29 Mora VT 4807

9.3 Fixation by epoxy resin

Epoxy resin and hardener were used for test sample fixation. First test samples were cut then samples were set into template. After that epoxy resin with hardener were mixed and gently filled template and then epoxy resin were hardened for 24 hours.

For fixation was used:

- o Epoxy resin BUEHLER EPOXICURE RESIN 20-8130-032
- o Epoxy hardener BUEHLER EPOXICURE HARDENER 20-8132-008

Fig.30 BUEHLER EPOXICURE Products

9.4 Grinding

Test sample grinding was made on grinder BUEHLER EcoMet 250 PRO. Test samples were grinded in few steps, first using grinding wheels of different grit sizes and then following finish grinding by using diamond suspension.

Fig.31BUEHLER EcoMet 250 PRO[11]

Parameters:

-Contact force 25   N

-Speed of samples   30   RPM

-Canvas speed   300   RPM

10 MEASURING DEVICE PARAMETERS

10.1 DSI method parameters

For DSI method was used MicroCombi Tester from CSM Instruments according to standard CSN EN ISO 14577-1.

Test parameters:

- o Applied forces- 0,5N; 1N; 5N
- o Sustain at maximal load 90s
- o Loading and unloading speed -1N/min for 0,5N load,2N/min for 1N, 10N/min for 5N load
- o Poisson number 0,3

As indenter was used four-sided diamond pyramid with tip angle 136°- Vickers indenter. Measurement was performed by DSI-Depth Sensing Indentation and for evaluation of micro-mechanical properties was used Oliver & Pharr method.

Fig.32 Micro-hardness tester- Micro Combi Tester [11]

10.2 X-ray diffraction Parameters

For measurement was used device X´Pert PRO from company PANalytical (Netherlands). Device is equipped with x-ray emitter CuKα, Ni filter and fast linear positional sensitive detector X´Celerator. At measurement was used Bragg-Brentatn configuration, voltage 40kV, current 30mA. Measurement was performed in range $2\theta=5°-30°$.

Fig.33X´Pert PRO

11 RESULTS

Five measurements were performed for each sample by DSI- the depth sensing indentation and WAXS- Wide Angle X-ray Scattering was used for observing structure of polymer. Obtained results were evaluated and illustrated by boxplot diagrams.

11.1 Micro mechanical properties of annealed samples at 0,5N load

Graphical representation in Fig.34, which characterizes dependence of the indentation force on indentation depth, shows that properties of PLA before and after annealing process were changed. Hardness increasing was manifested by the shift of curves closer to lower indentation depths. In the Fig 34 is clear that the PLA sample which was annealed by temperature of 110°C had the highest hardness and the PLA with annealing temperature of 130° had C the lowest hardness.
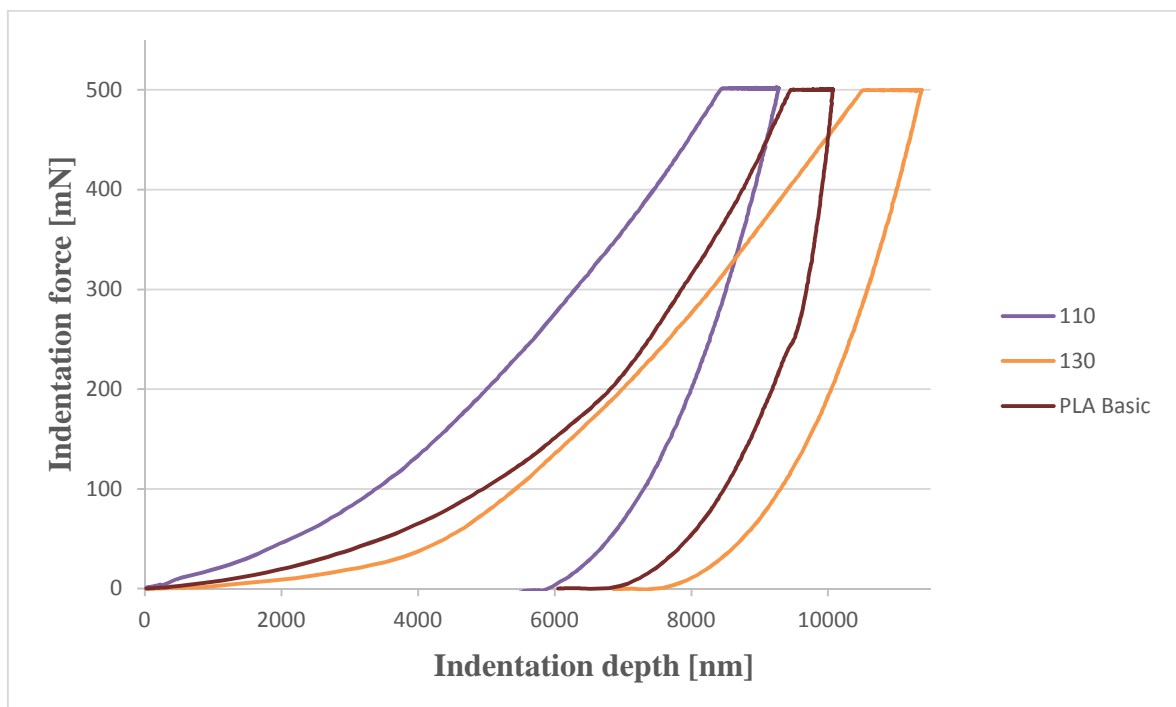
Fig.34 *Dependence indentation force on indentation depth measured at 0,5N load*

Next Fig.35 represents dependence of indentation depth on indentation time, light increase of indentation depth was apparent at the beginning of indentation, it was caused by very slow indentation loading. In Fig 35 beginning of creep was clearly seen that when in range of 20 to 40 s load reached maximum, remains for some time constant with indentation depth changing. Indentation curves give opportunity to obtain values of indentation hardness, indentation modulus and size of deformation elastic, plastic and total work required

to create indentation, dependence of dependence of indentation depth on indentation time is important for determination creep behavior of polymers.
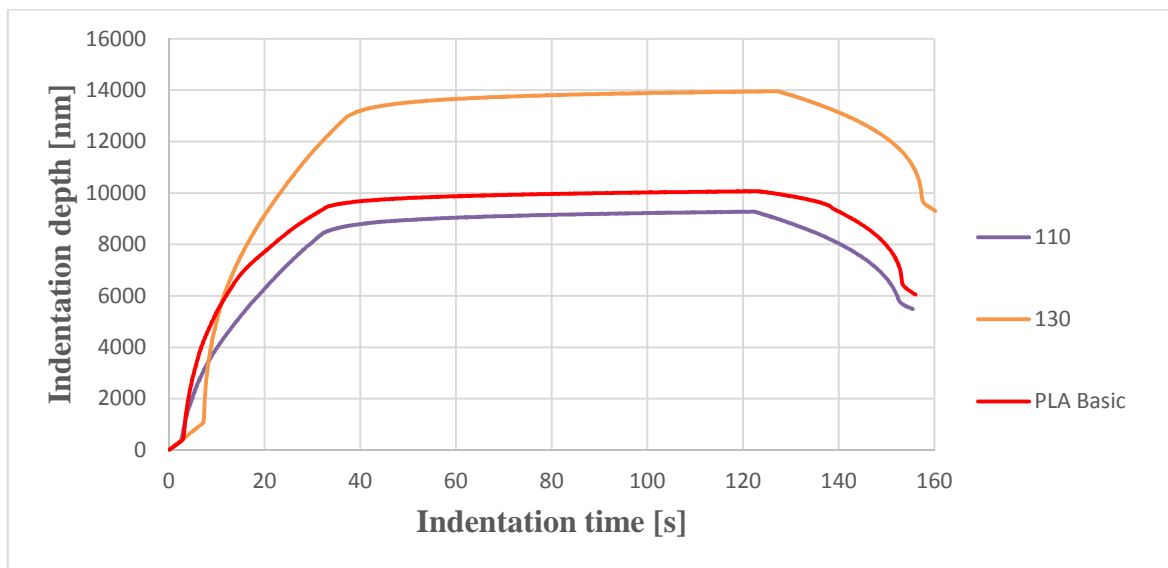
Fig.35 Dependence indentation depth on indentation time measured at 0,5N load

11.1.1 Indentation hardness

Indentation hardness is basic quantity obtained by depth sensing indentation. Indentation hardness is resistance to permanent deformation or damage and it is defined as quotient of the maximum load force to projection of the contact area.

From measured results Fig.36 was clearly seen that PLA basic was sample with highest value of indentation hardness (265,1MPa) and the lowest value was within PLA that was annealed by temperature of 90°C(197,4MPa). Difference between the highest and lowest value of indentation hardness was 26%.
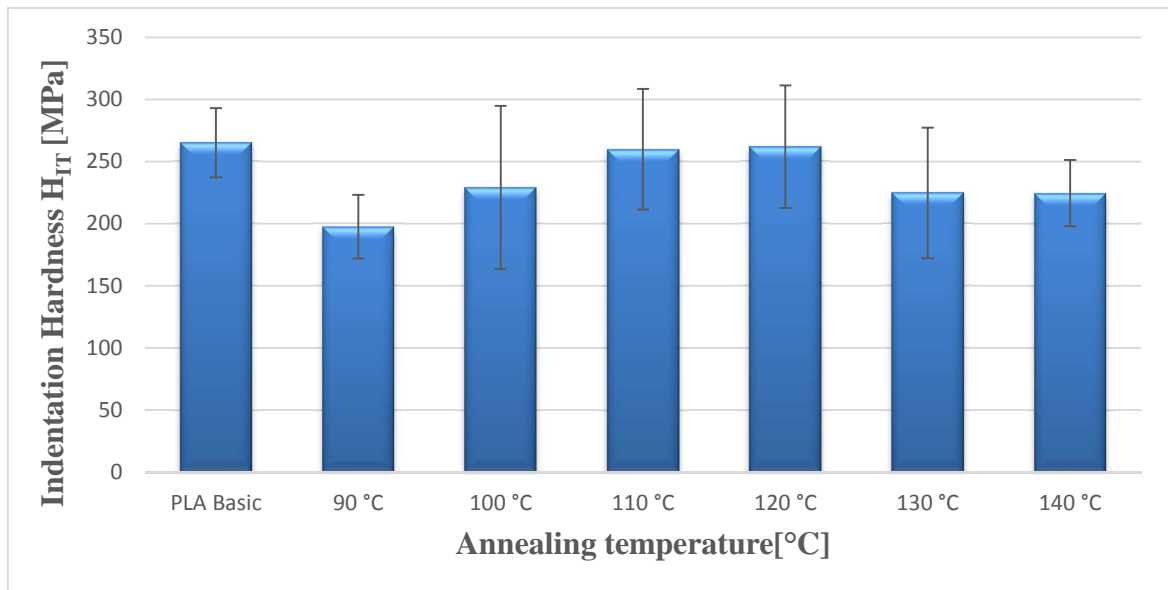
Fig.36 Indentation hardness measured at 0,5N load

11.1.2 Indentation modulus

Another important quantity, which we can obtain from DSI, is indentation modulus. It is determined form slope of the tangent unloading curve and corresponds to elastic modulus.

The highest value of indentation modulus was identified within PLA Basic (9,4 GPa) results shown in Fig. 37, and PLA that was annealed by temperature of 90°C had the lowest value of indentation modulus (4,3 GPa), between the highest and lowest value of indentation modulus was 50% difference.
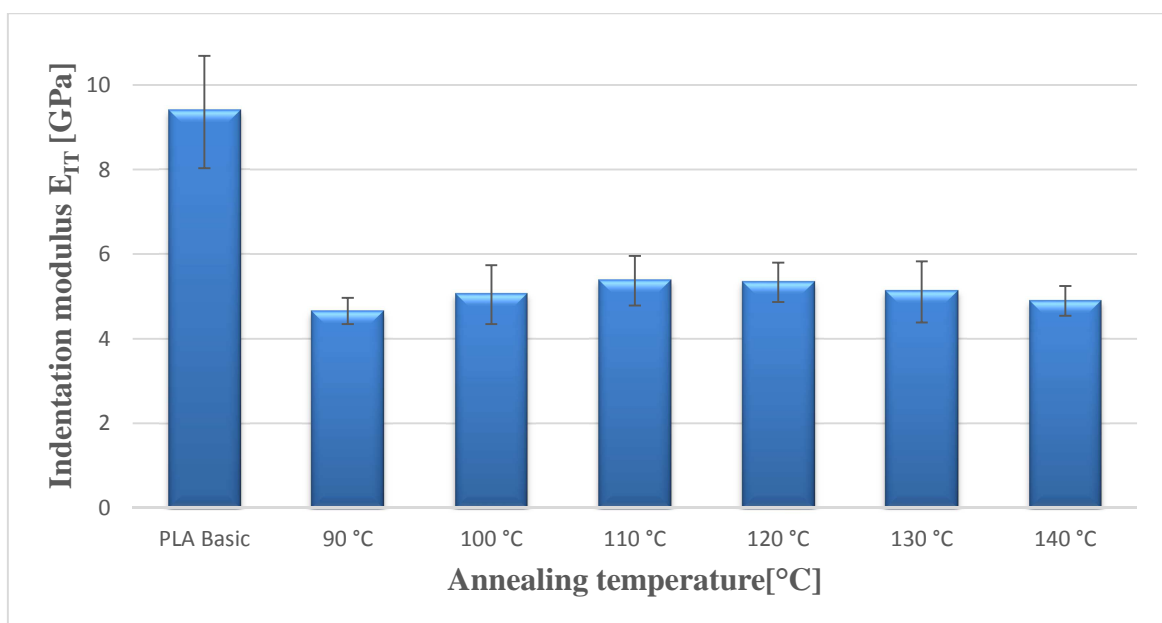
Fig.37 Indentation modulus measured at 0,5N load

11.1.3 Deformation work

Elastic deformation work of indentation was obtained from measured values in Fig 38 and the highest value of measured samples had PLA annealed by temperature of 140^0C (625318 μJ) and PLA Basic (460003 μJ) had the lowest value, difference between values the highest and the lowest of elastic deformation work was 26%.

The highest value plastic deformation work of indentation had PLA annealed by temperature of 140^0C (1591563μJ) and the lowest measured value had PLA Basic (1208321 μJ), difference between the highest and the lowest values of plastic deformation work was 36%.

PLA annealed by temperature of 120^0C (30,4 %) was the PLA sample with the highest relaxation coefficient value and the lowest value of relaxation coefficient was within PLA annealed by temperature of 140^0C (28,3 %) so the difference between these values was 7%.
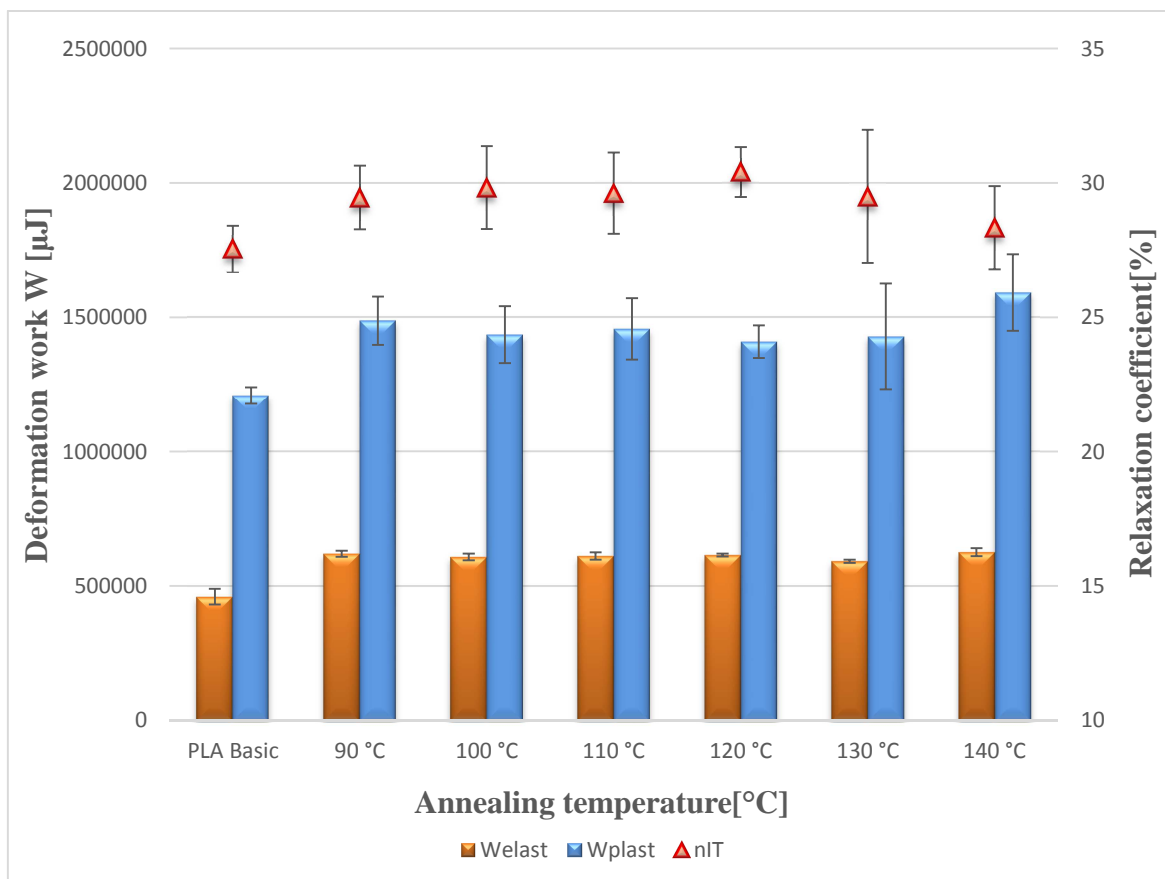
Fig.38 Deformation work and relaxation coefficient measured at 0,5N load

11.1.4 Indentation creep

It was apparent from measured values that in Fig. 39 the highest value of indentation creep had sample that was measured within PLA annealed by temperature of 110^0C (9,1%), and PLA Basic was sample with the lowest value has (6,8%), difference between the highest and the lowest values of indentation creep was 25 %.
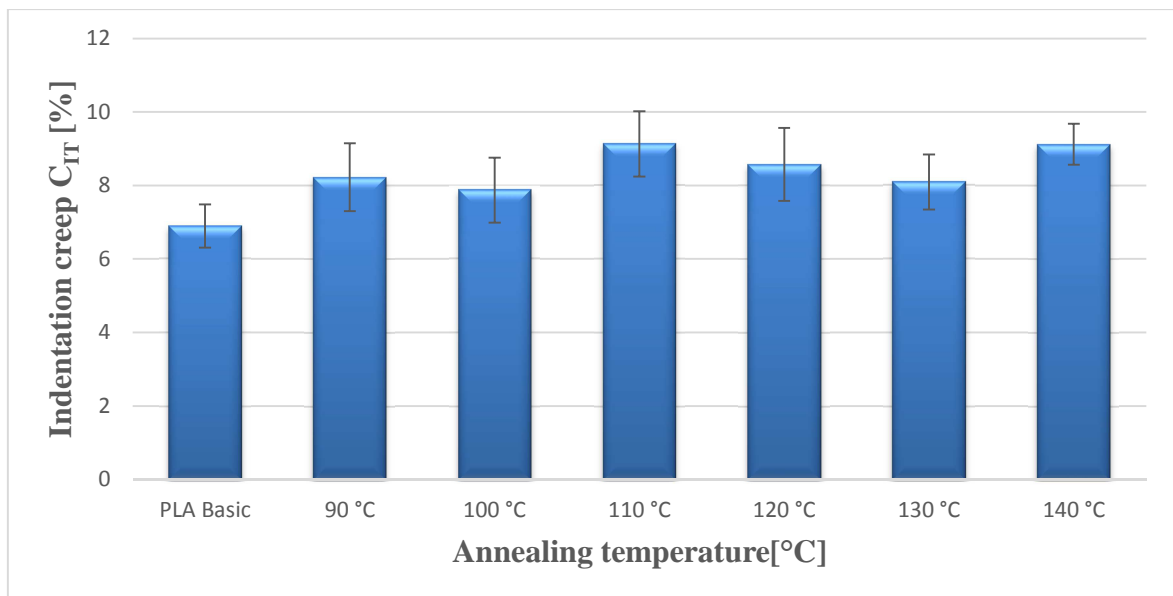
Fig.39 Indentation creep measured at 0,5N load

11.1 Micro mechanical properties of annealed samples at 1N load

Properties change of PLA before and after annealing process was apparent in graphical representation Fig. 40, which characterizes dependence of indentation force on indentation depth. Increased hardness manifests by shift of curves closer to lower indentation depths. Also decreased area under curve was decreasing, which represents total mechanical indentation work, which confirms other diagrams. In Fig. 40, was apparent that the highest hardness had sample annealed by temperature of 110 °C and the lowest basic material right after injection molding PLA Basic.
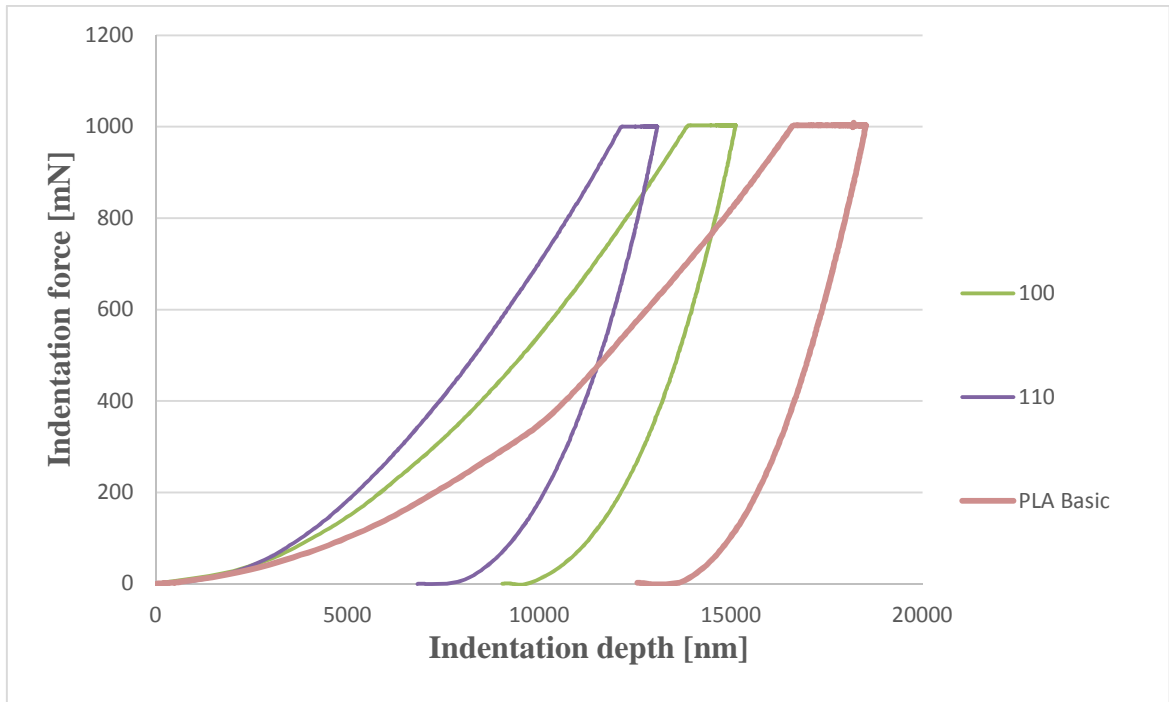
Fig.40 Dependence indentation force on indentation depth measured at 1N load

Following Fig. 41 was dependence of indentation depth on indentation time, in the beginning of indentation was apparent moderate increase of indentation depth, it was caused by very slow indentation loading. In Fig. 41 was clearly seen beginning of creep when in range of 20 to 40 s load reaches its maximum and remains for some time constant with indentation depth changing.
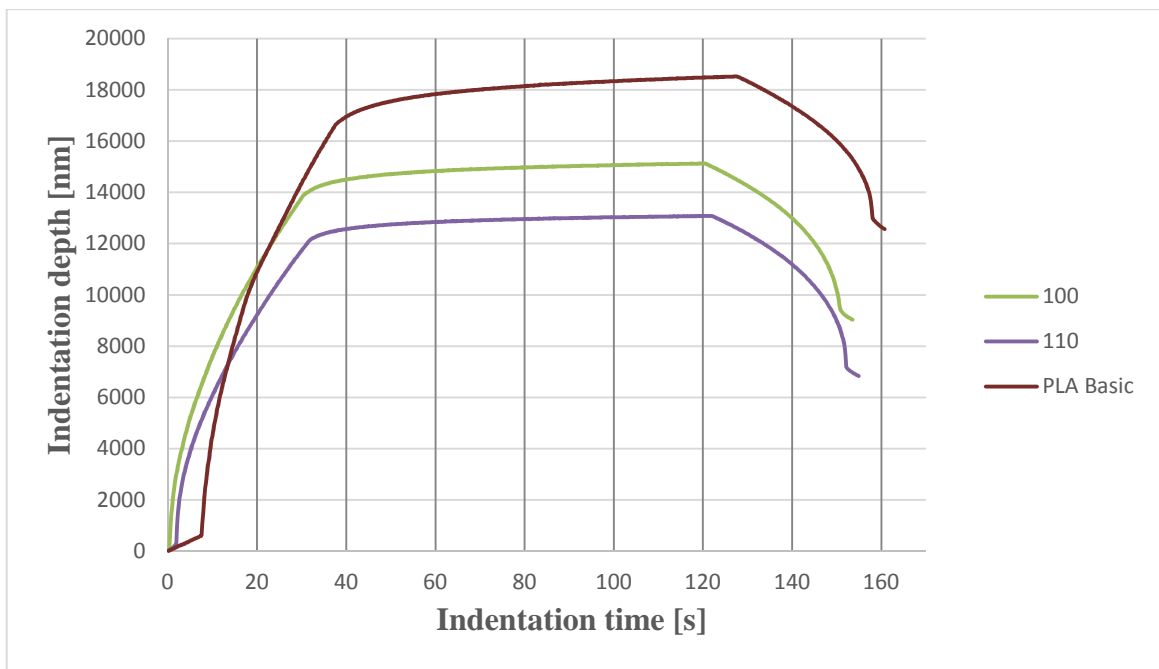
Fig.41 Dependence indentation depth on indentation time measured at 1N load

11.1.1 Indentation hardness

The highest value of indentation hardness had PLA that was annealed by temperature of $100^{0}C$ (244,5MPa) as seen from measured results Fig.36 and the PLA Basic (190,8MPa) had the lowest value of indentation hardness. Difference between the highest and lowest value of indentation hardness was 22%.
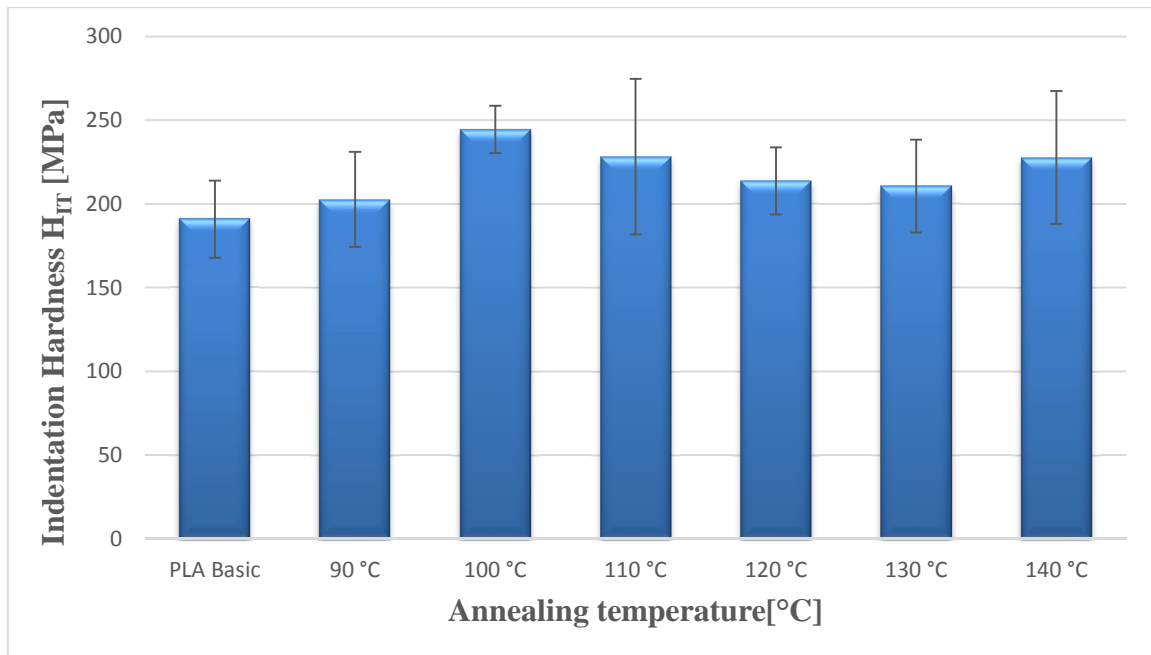
Fig.42 Indentation hardness measured at 1N load

11.1.2 Indentation modulus

The highest value of indentation modulus was identified within PLA annealed by temperature of $100^{0}C$ (5,1 GPa) results measured Fig. 43 and sample of measured PLA Basic (4,4 GPa) had the lowest value of indentation modulus, between the highest and lowest values of indentation modulus was 14% difference.
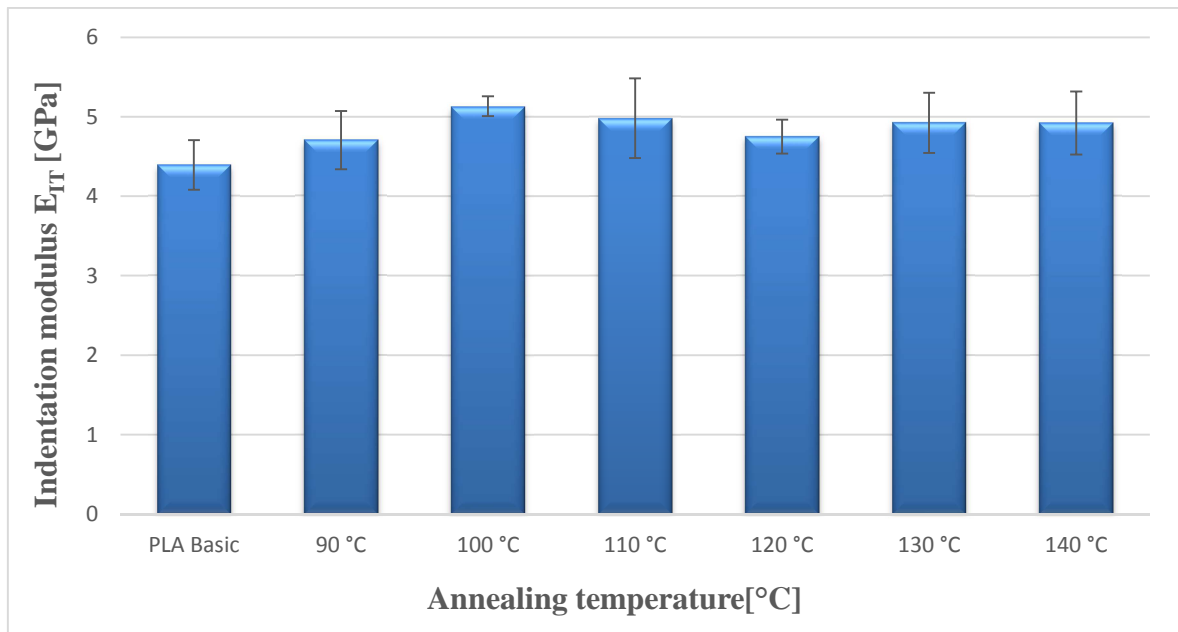
Fig.43 Indentation modulus measured at 1N load

11.1.3 Deformation work

Elastic deformation work of indentation was obtained from measured values in Fig 44 and the PLA annealed by temperature of 140^0C (1768027 μJ) had the highest value of measured samples had and PLA Basic (1680861 μJ) had the lowest value, difference between values the highest and the lowest of elastic deformation work was 5%.

The highest value plastic deformation work of indentation was within PLA Basic (5303497μJ) and PLA annealed by temperature of 100^0C (3923571 μJ) had the lowest measured value, difference was 26% between the highest and the lowest values of plastic deformation work.

The PLA sample with the highest relaxation coefficient value was PLA annealed by temperature of 100^0C (31,1 %) and the lowest value of relaxation coefficient was within PLA Basic (24,1 %) so the difference between these values was 22%.
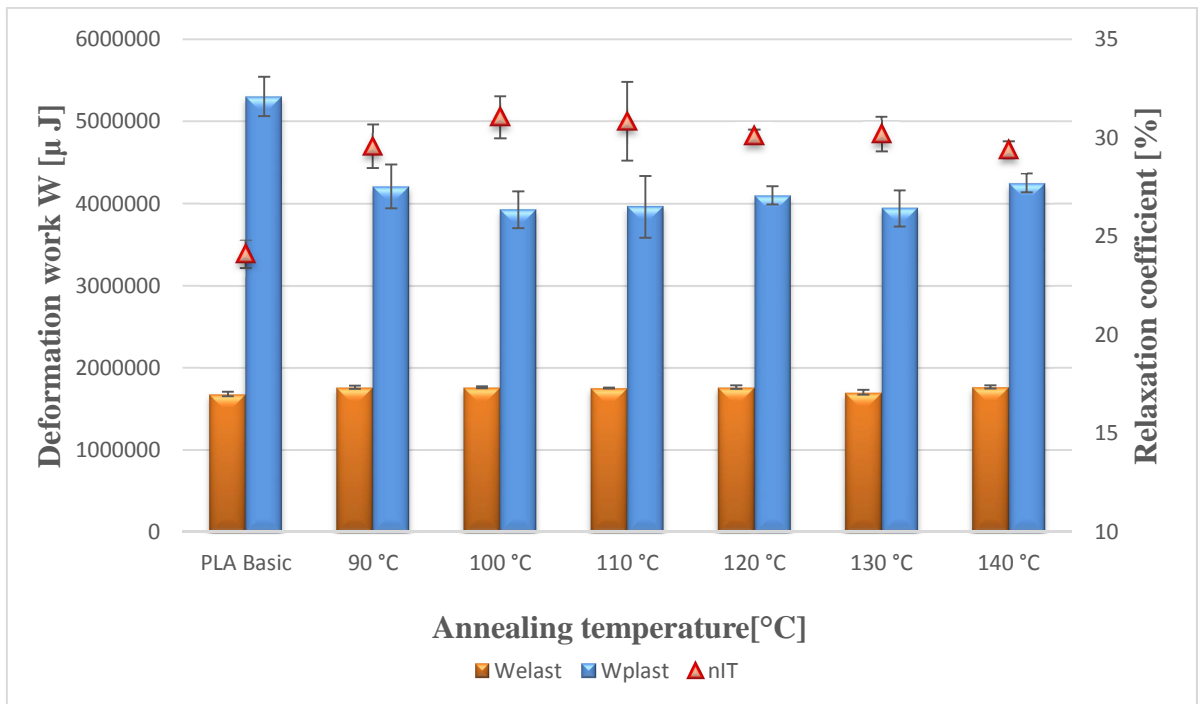
Fig.44 Deformation work and relaxation coefficient measured at 1N load

11.1.4 Indentation creep

From measured values was apparent that in Fig. 45 the highest value of indentation creep sample that was measured within PLA Basic (11,7%), and PLA annealed by temperature of 130^0C had the lowest value of indentation creep (7,6%), difference between the highest and the lowest values of indentation creep was 35%.
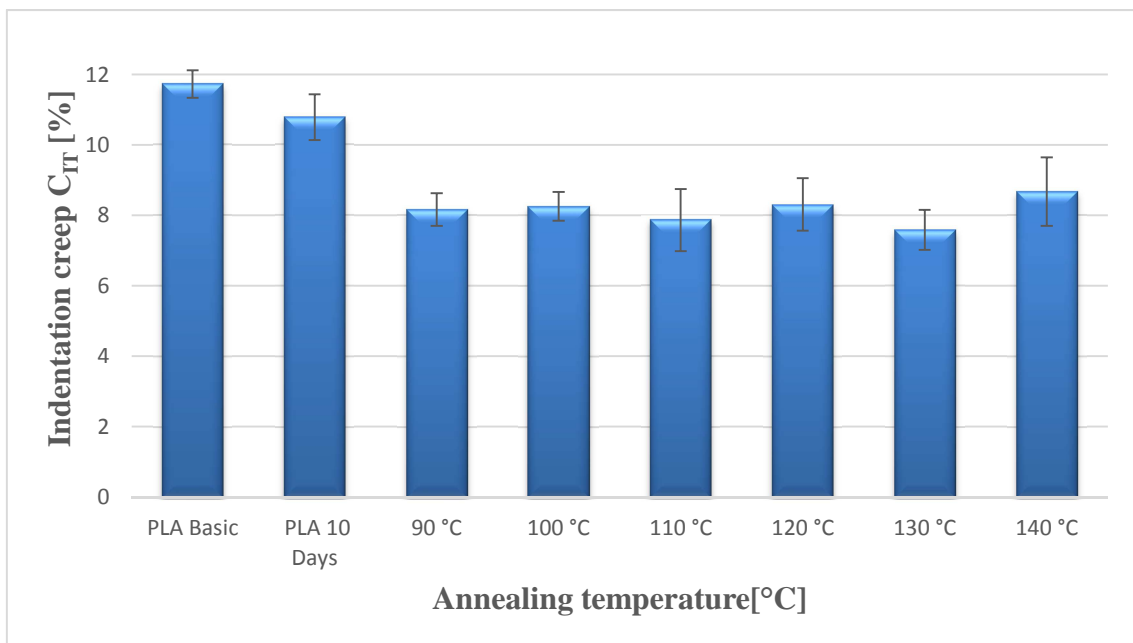
Fig.45 Indentation creep measured at 1N load

11.2 Micro mechanical properties of annealed samples at 5 N load

It was apparent from graphical representation Fig.46, which characterizes dependence of indentation force on indentation depth, that properties of PLA before and after annealing process were changed. Increase of hardness was manifested by shift of curves closer to lower indentation depths. In the Fig.46 was clear that sample of PLA annealed by temperature of 100°C had highest hardness and lowest hardness was PLA annealed by temperature of 90°C.
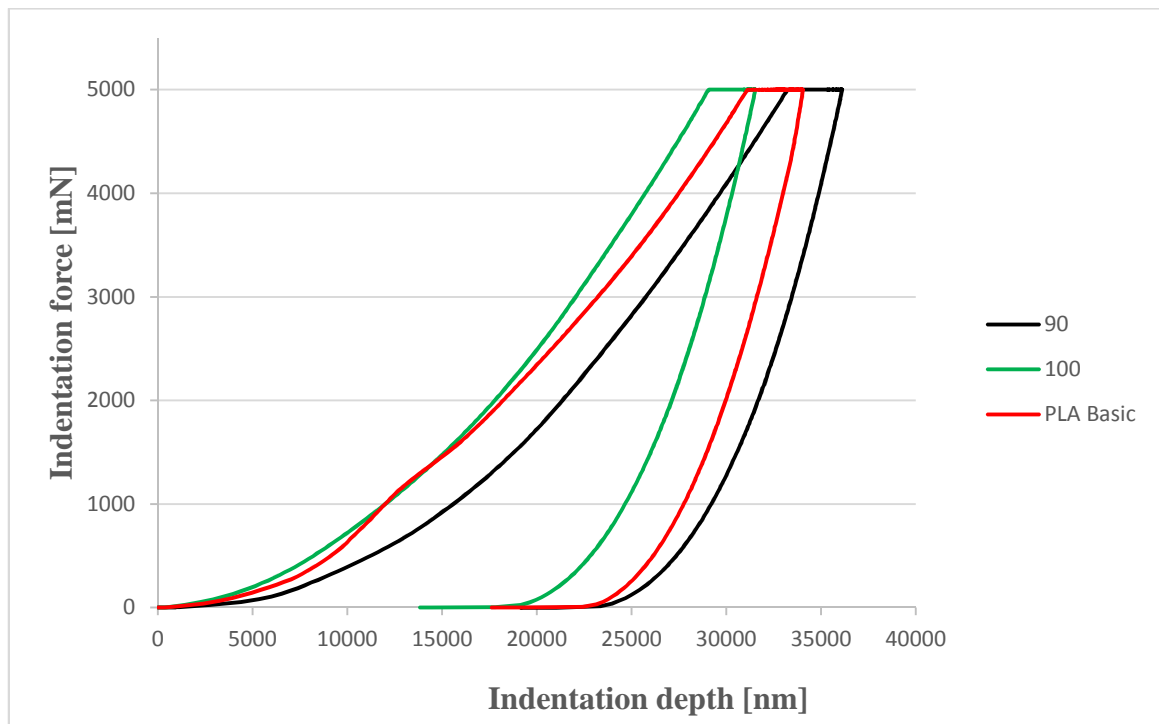
Fig.46 Dependence indentation force on indentation depth measured at 5N load

Following Fig. 47 was dependence of indentation depth on indentation time, the moderate increase of indentation depth was apparent in the beginning of indentation, it was caused by very slow indentation loading. In Fig. 47, beginning of creep was clearly seen that when in range of 20 to 40 s load reaches its maximum and remains for some time constant with indentation depth changing. It was clear that annealing influence indentation creep of PLA.
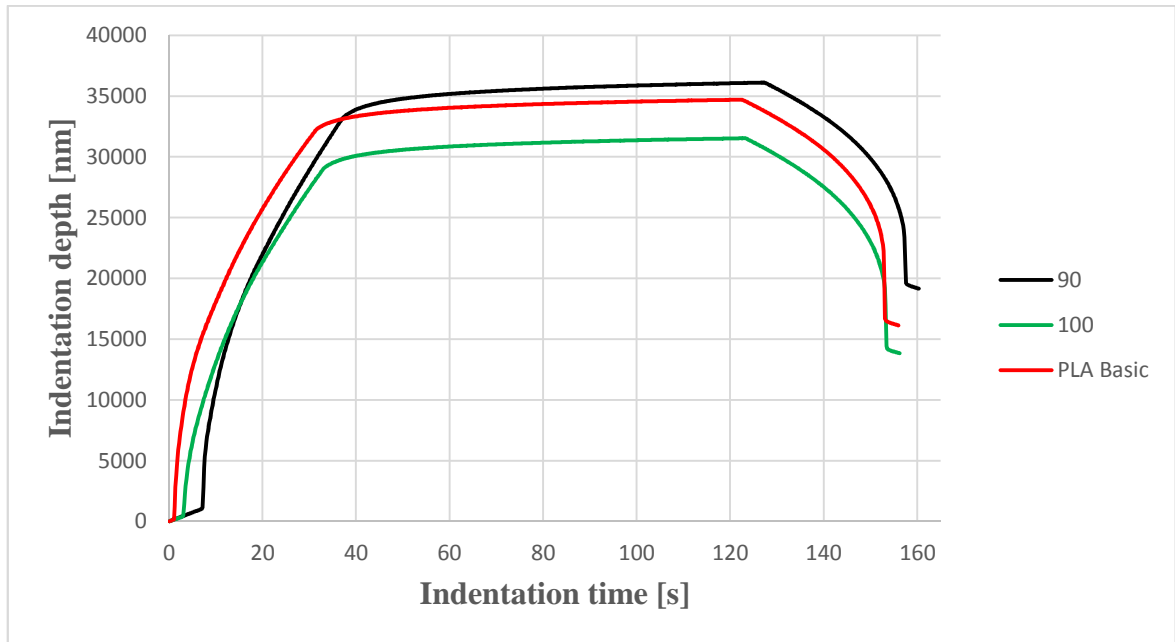
Fig.47 Dependence indentation depth on indentation time measured at 5N load

11.2.1 Indentation hardness

From measured results Fig.36 is apparent that sample with the highest value of indentation hardness (218,7MPa) was the PLA annealed by temperature of 110^0C and the lowest value was within PLA that was annealed by temperature of 90°C(188,4MPa). Difference between the highest and lowest value of indentation hardness was 14%.
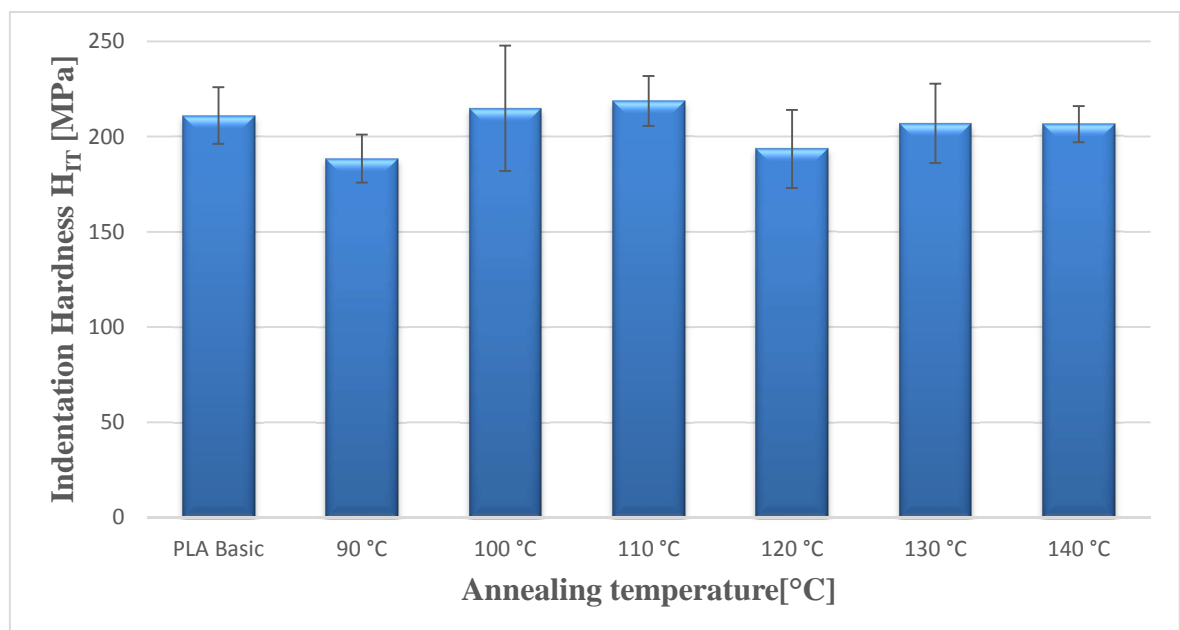

Fig.48 Indentation hardness measured at 5N load

11.2.2 Indentation modulus

The highest value of indentation modulus was identified within PLA Basic (4,9 GPa)results measured Fig. 49 and PLA that was annealed by temperature of 110°C had the lowest value of indentation modulus (3,6GPa) between the highest and the lowest value of indentation modulus was 25% difference.
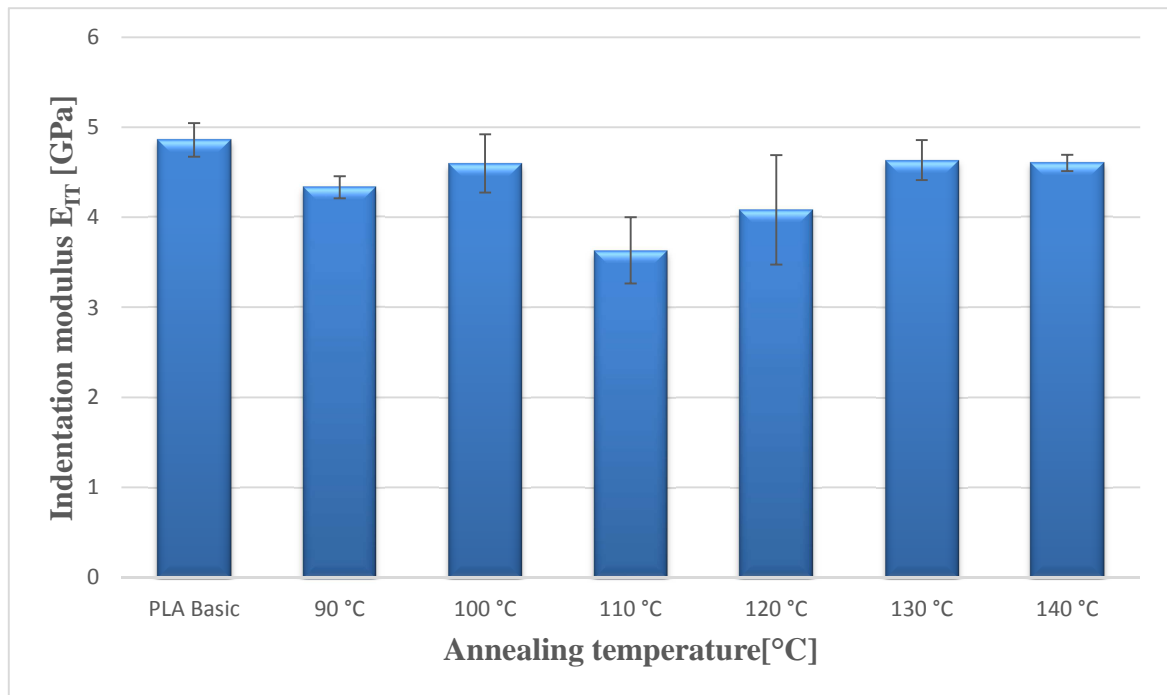
Fig.49 Indentation modulus measured at 5N load

11.2.3 Deformation work

Elastic deformation work of indentation was obtained from measured values in Fig 50 and the highest value of measured samples was PLA annealed by temperature of 110^0C (24008165μJ) and PLA Basic (18684059μJ) had the lowest value of deformation work, difference between values the highest and the lowest of elastic deformation work was 22%.

The PLA Basic (51253939 μJ) had the highest value plastic deformation work of indentation and PLA annealed by temperature of 110^0C (43902369 μJ) had the lowest value, difference between the highest and the lowest values of plastic deformation work was 14%.

PLA annealed by temperature of 110^0C (35,4 %) was the PLA sample with the highest relaxation coefficient value and the lowest value of relaxation coefficient was within PLA Basic (26,8 %) so the difference between these values was 24%.
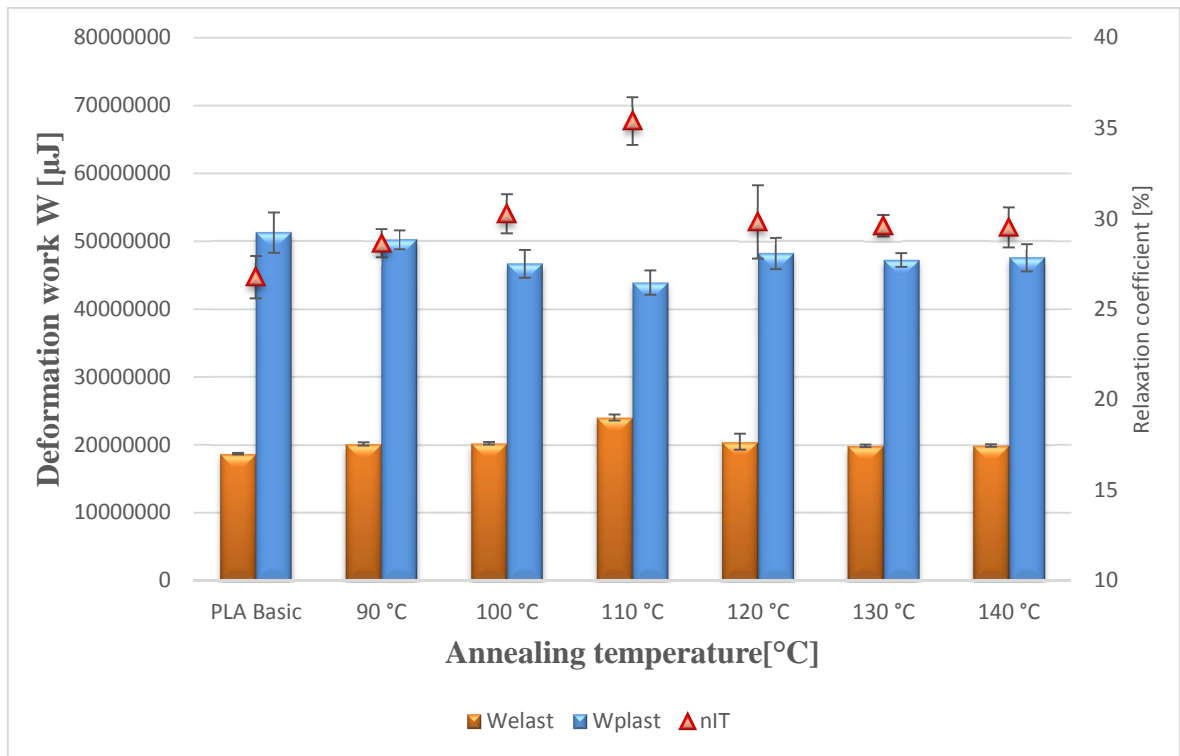
Fig.50 Deformation work and relaxation coefficient measured at 5N load

11.2.4 Indentation creep

From measured values was apparent that in Fig. 51 the highest value of indentation creep had sample that was measured within PLA Basic (8,7%), and PLA annealed by temperature of 120^0C was sample with the lowest value of indentation creep (7,3%), difference between the highest and the lowest values of indentation creep was 15%.
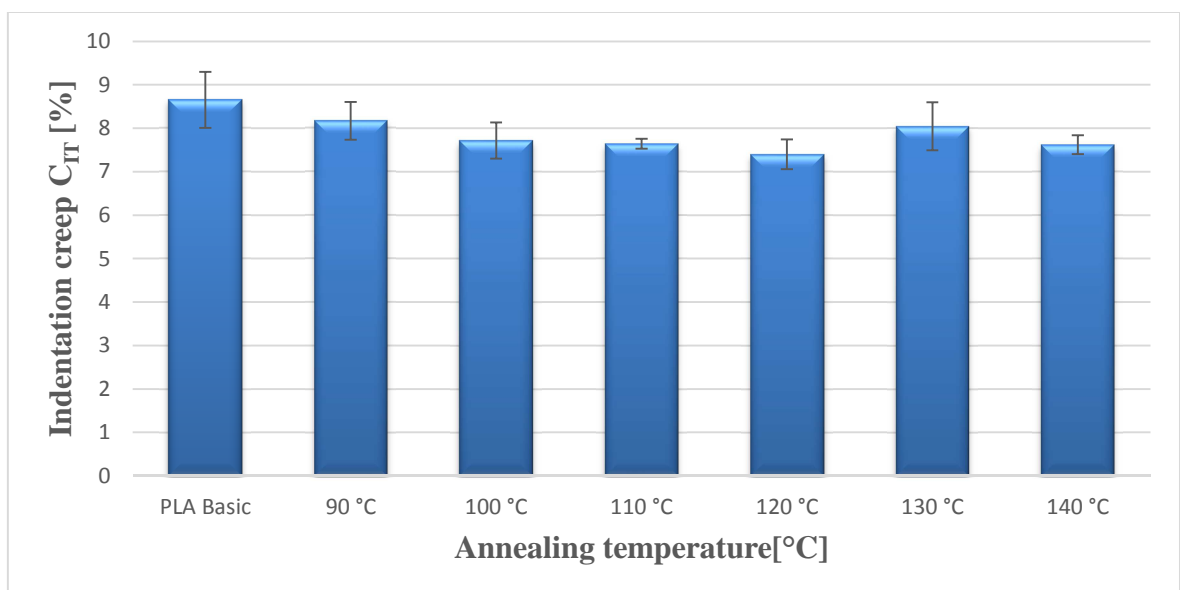

Fig.51 Indentation creep measured at 5N load

11.3 Annealed samples crystallography

Table 3 Measured crystallinity and size of spherulites

	PLA	90 °C	100 °C	110 °C	120 °C	130 °C	140 °C
Amorphous Phase [%]	100	46	48	44	47	39	41
Crystalline Phase [%]	0	54	52	56	53	61	59
Spherulites Size [μm]		346	388	320	372	282	350

With wide angle x-ray diffraction was measured change of content crystalline and amorphous phase the surface and center of the tested polymer in our case PLA.
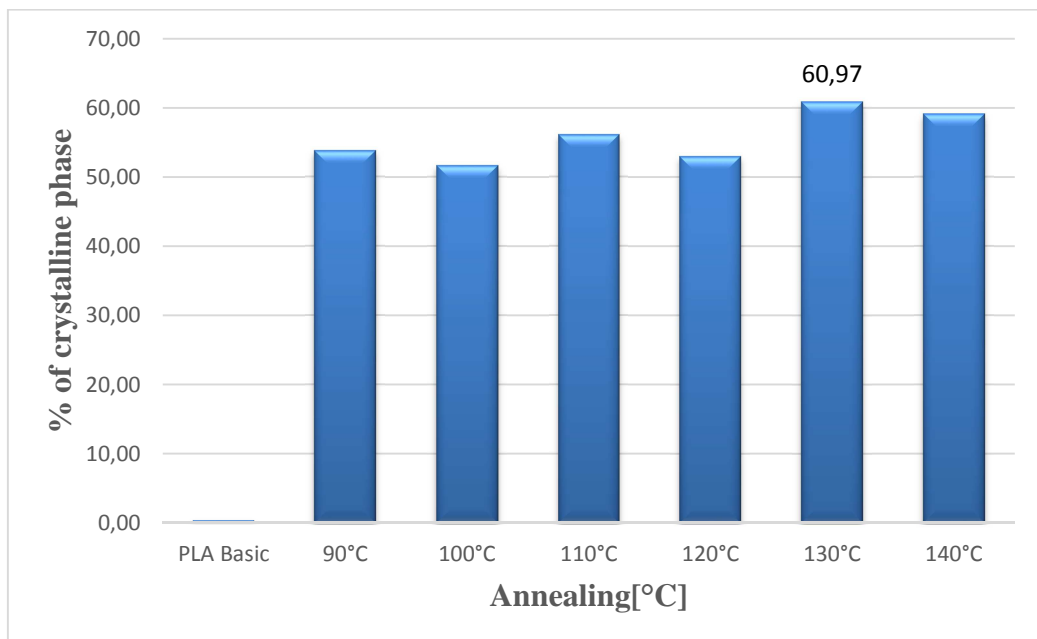
Fig.52 The proportion of crystalline phase

It was apparent from the measured results of wide angle x-ray diffraction that the highest amount of crystalline phase has PLA annealed by temperature of 130^0C. Also was apparent from measured results Fig. 52 and Fig. 53 that effect of annealing was increasing crystallinity of PLA. The size of spherulites is also changing and had certain influence on properties.
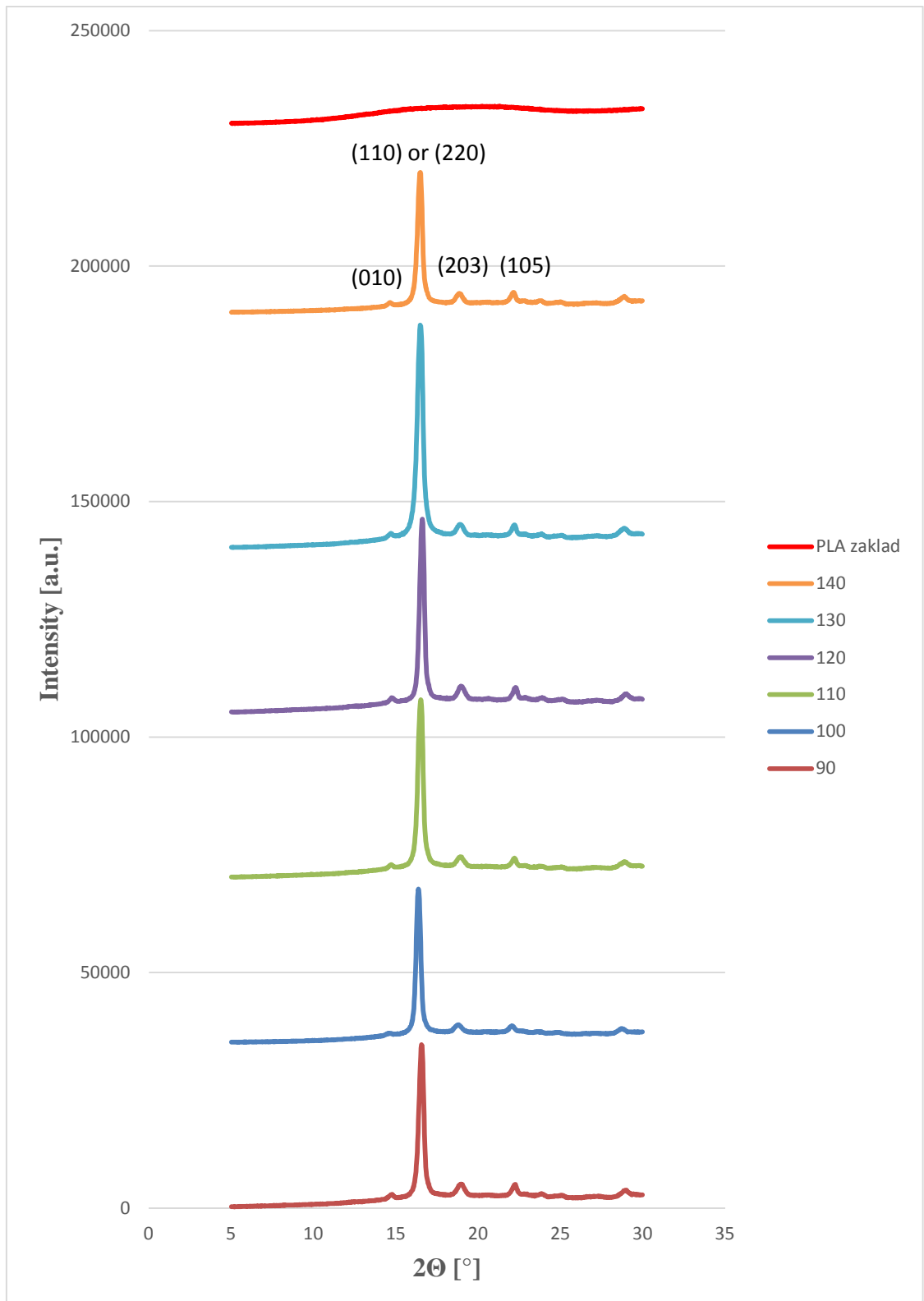
Fig.53 Shift of X-ray diffraction curves

It was apparent in Fig. 54 that the PLA change of crystallinity content from pure amorphous to crystalline.

12 RESULT DISCUSSION

The master thesis deals with micromechanical properties measurement of coating modified PLA. Test samples were prepared injection molding technology at the injection molding machine ARBURG ALLROUNDER 470 C and then annealed by temperatures of 90, 100, 110, 120, 130 and 140°C. Micromechanical properties changes of coating annealed PLA were measured by DSI- Depth Sensing Indentation method at applied loading 0.5, 1 and 5N. Measured values were graphically represented and evaluated. For easier orientation was used so-called dimensionless units express as ratio of each measurement to maximal value of basic (non-modified) PLA in each measurement process.

12.1 Indentation hardness at different load forces
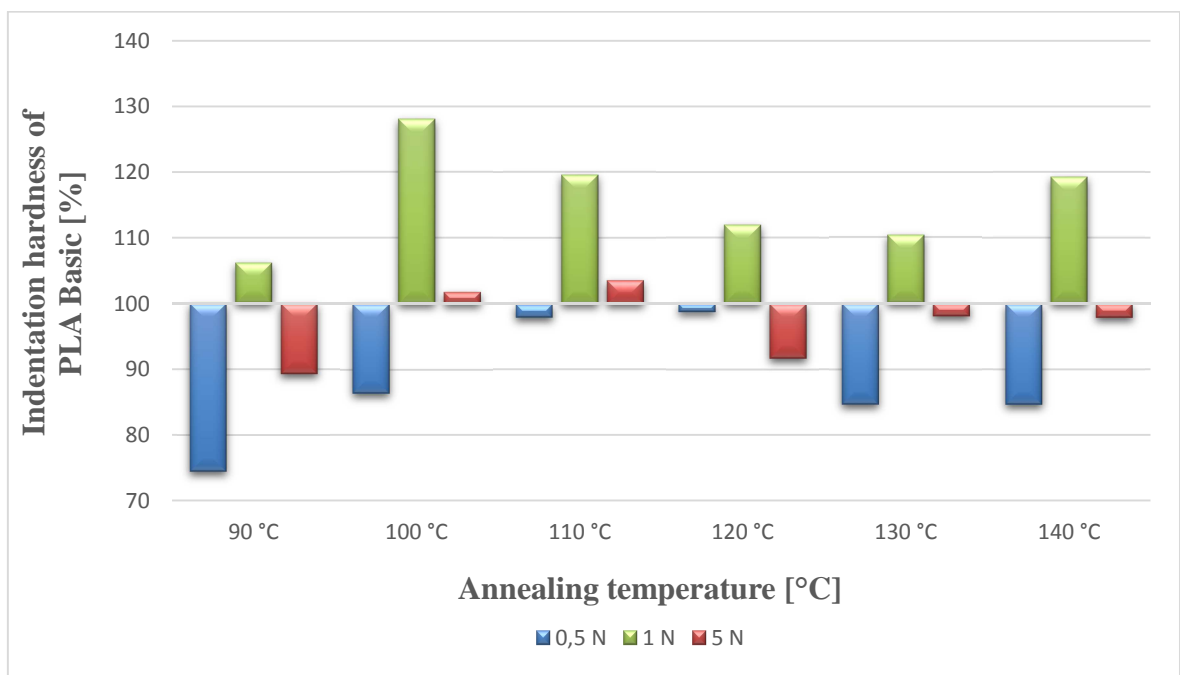
Fig.54 Comparison of PLA Basic indentation hardness H_{IT} to annealed materials

Graphical evaluation of indentation hardness measured PLA Basic results percentile compared to PLA in dependence on different annealing temperature and various loading forces were shown in Fig. 54.

From measured results of microhardness PLA was apparent that the highest values of indentation hardness were achieved within PLA annealed by temperature of 100°C. Vice versa the lowest values were achieved for PLA annealed by temperature of 90°C. Differences in applied loads most significantly were reflected for PLA annealed by temperature of 100°C. While using smallest load (0,5N), was apparent that within all in-

dentation hardness measurements were decreased values. Vice versa during measurement of indentation hardness, where was used loading 1N, was apparent increase values of all indentation hardness tests.

The increase of indentation hardness values at load 1N was achieved compared to basic non-annealed PLA by 30%, similarly as the decrease values at applied load 0,5N. Such differences could be caused by different structure of annealed PLA. From measurement WAXS-Wide Angle X-ray Scattering is apparent that the crystallinity change can significantly influence behavior of surface layer on the transition amorphous and crystalline phase. Also size of spherulites played important part during indentation hardness measurements of surface layer annealed PLA.

12.2 Indentation modulus at different load forces
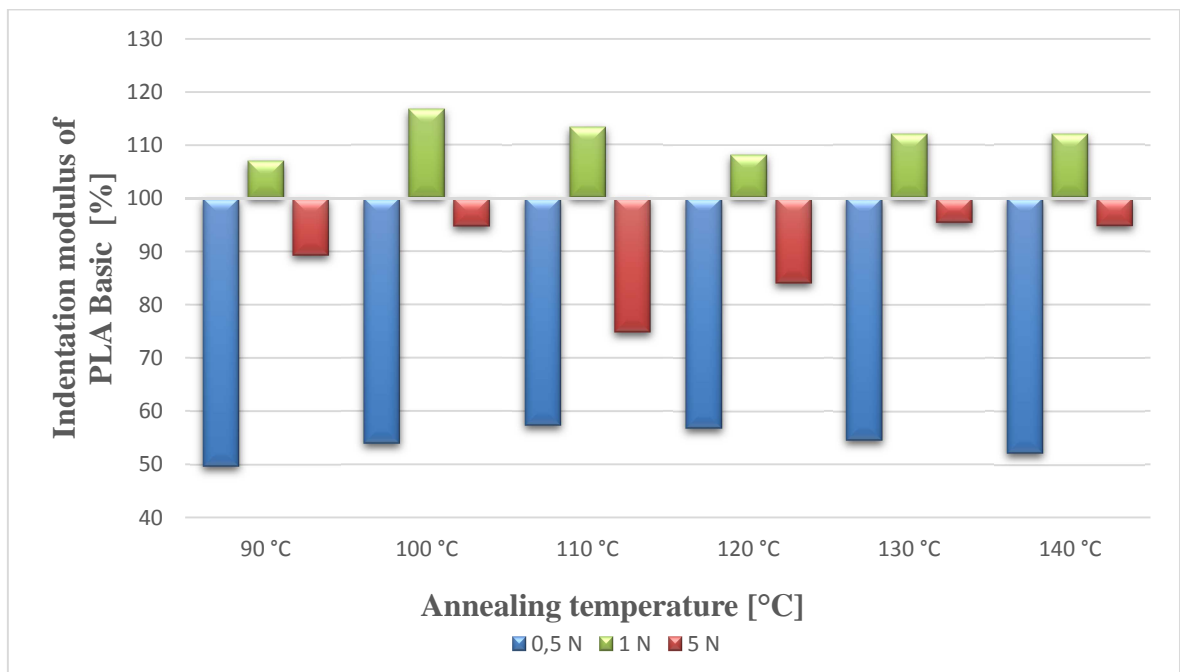
Fig.55 Comparison of PLA Basic indentation modulus E_{IT} to annealed materials

Graphical percentile comparison of PLA Basic indentation modulus to PLA annealed by various temperatures at different loading forces was shown in Fig. 55.

It was apparent from the PLA microhardness measurements that the highest values of indentation modulus were measured for PLA annealed by temperature of 100°C. Vice versa the lowest values were achieved within PLA annealed by temperature of 90°C. Most significant differences in applied loads were reflected for PLA annealed by temperature of 100°C. At the lowest used load 0,5N was apparent that all measurements of indentation

modulus had decreased values. Vice versa, where was used load 1N load, during measurements of indentation modulus was apparent the increase of values at all measurements.

The increase of indentation modulus values compared to basic non-annealed PLA was 16% when was used load 1N, but the decrease of indentation modulus values was 50% at load 0,5N. Different structure of annealed PLA samples could cause these differences. From WAXS measurements is apparent that the changes of crystallinity could significantly influence surface layer behavior on the transition of crystalline and amorphous phase. Spherulites size also could be very important at microhardness measurements of surface layer annealed PLA.

12.3 Indentation creep at different load forces
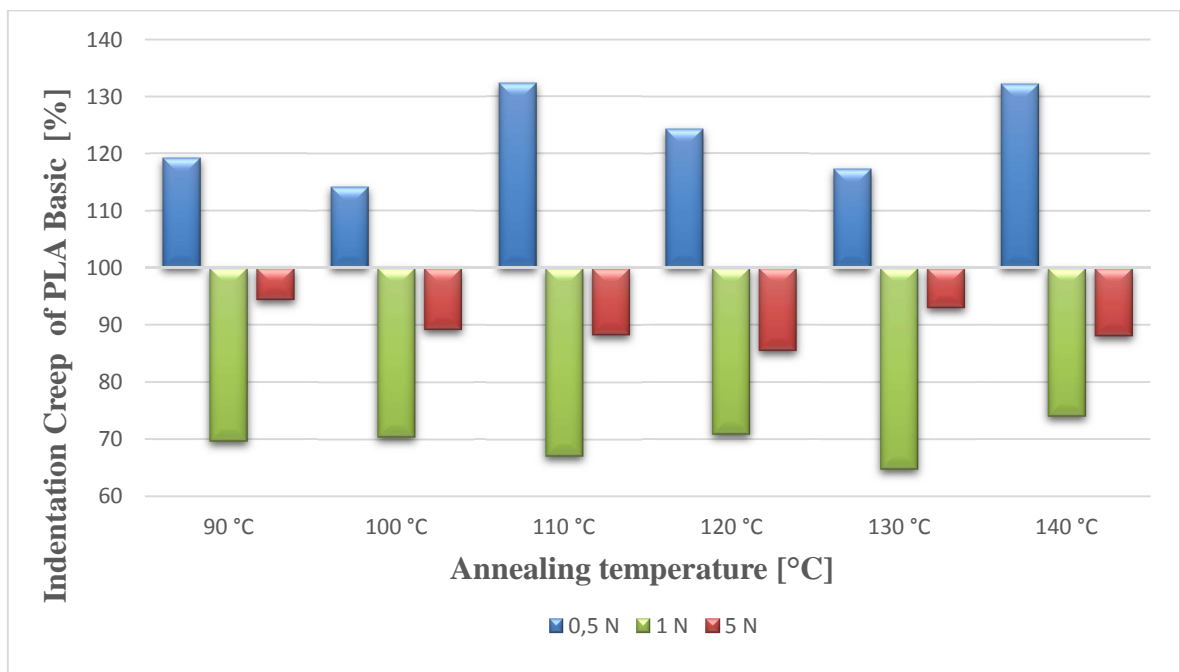
Fig.56 Comparison of PLA Basic indentation creep C_{IT} to annealed materials

Indentation creep PLA Basic percentile comparison was graphically evaluated in Fig. 56 and compared to different annealing temperatures and various loads.

The results of PLA microhardness measurements shown, that the highest indentation creep values were observed in PLA annealed by temperatures of 110 and 140°C. The lowest values were achieved on to contrary for PLA annealed by temperature of 130°C. Differences in applied load were most significantly reflected for PLA annealed by temperature of 110°C. When was used the smallest load 0,5N, it was apparent that all values of indentation creep measurements were increased. Vice versa all measured values of indentation

creep at 1N load were decreased. The increase of indentation creep values compared to basic non-annealed PLA was 32%, similarly as the decrease of indentation creep values at load 1N. From the WAXS is apparent that the crystallinity changes could significantly influence surface layer behavior on transition amorphous and crystalline phase, also size of spherulites could be very important to measurements microhardness of surface layer annealed PLA.
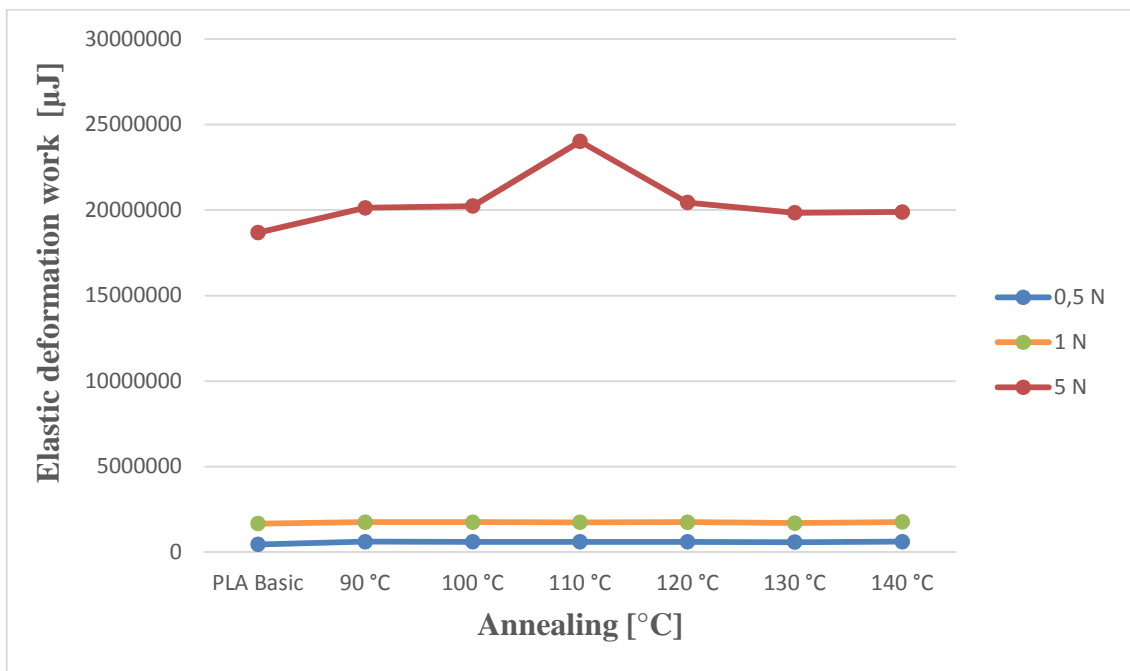
12.4 Elastic deformation work of indentation

Fig.57 Elastic deformation work of indentation W_{Elast} comparison

Elastic deformation work of indentation was identified in Fig.57 was the highest value within PLA annealed by temperature of 110°C at 5N load. The decreased values of elastic deformation work had PLA Basic.

12.5 Plastic deformation work of indentation
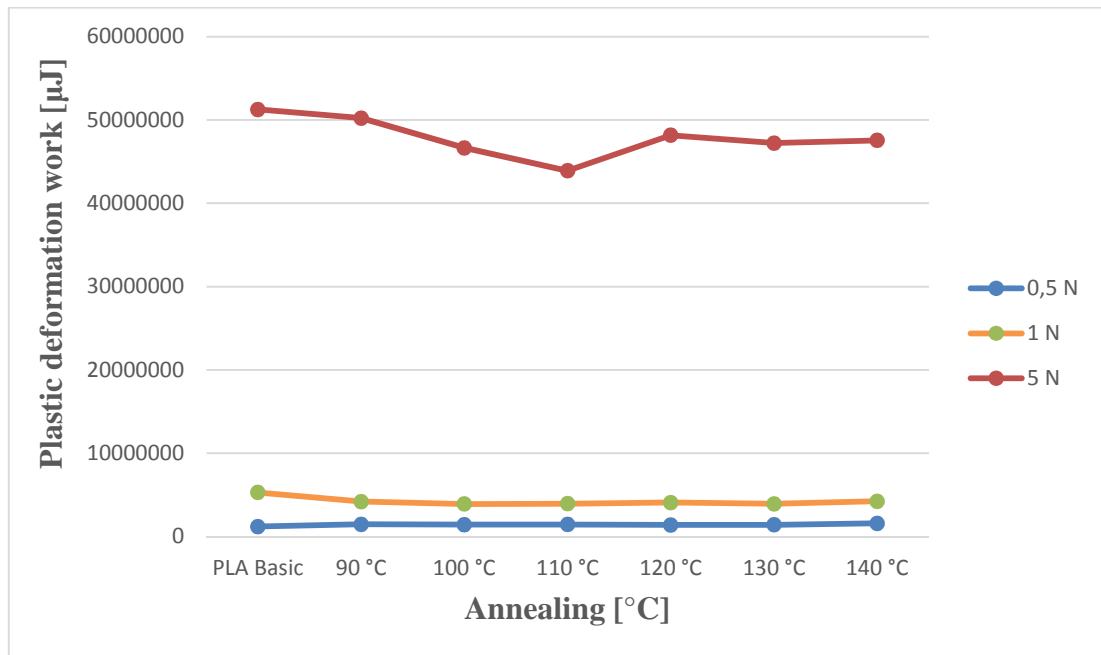
Fig.58 *Plastic deformation work of indentation W_{Plast} comparison*

The highest plastic deformation work of indentation value was within PLA Basic at 5N load and also PLA Basic at 0,5N load was sample with lowest value was shown in Fig. 58.

13 CONCLUSION

Aim of this master thesis was perform measurement of microhardness modified PLA polymer using DSI- Depth Sensing Indentation by MicroCombi tester.

Test samples were prepared injection molding technology at the injection molding machine ARBURG ALLROUNDER 470 C and then samples were modified by annealing temperatures of 90, 100, 110, 120, 130, 140 °C. Changes of micromechanical properties of surface layer annealed PLA were measured by the DSI-Depth sensing indentation. Test samples were measured by the loading forces of 0,5 N, 1 N, 5 N. On each test sample was measurement performed 5 times. Then results were evaluated and presented graphically. For easier orientation was used so-called dimensionless units express as ratio of each measurement to maximal value of basic (non-modified) PLA in each measurement process.

From measured samples can be determined that the values of indentation hardness H_{IT} can differ, depending on loading force. The highest value of indentation hardness was measured within PLA annealed by temperature of 100°C. Differences of applied loads values were most significantly reflected for PLA annealed by temperature of 100°C. The increased values of indentation hardness were observed, considering applied loads, at 1N load and the highest increase of indentation hardness values at load 1N that was achieved compared to basic non-annealed PLA, was 30%. It was apparent from all measurements that the crystallinity change can significantly influence behavior of surface layer on the transition amorphous and crystalline phase.

The highest value of indentation modulus E_{IT} was the PLA annealed by temperature of 100°C. The differences of applied loads values were most significantly reflected for PLA annealed by temperature of 100°C. The increased values of indentation modulus were observed, due to applied loads, at 1N load and the highest increase of indentation hardness values at load 1N that was achieved compared to basic non-annealed PLA, was 16%. Also was apparent from all measurements that the crystallinity change can significantly influence behavior of surface layer on the transition amorphous and crystalline phase.

The results of PLA microhardness measurements shown, that the highest indentation creep C_{IT} values were observed in PLA annealed by temperatures of 110 and 140°C. Differences in applied loads values were most significantly reflected for PLA annealed by temperature of 110°C. The increased values of indentation creep were observed, due to applied loads, at 0,5N load and the highest increase of indentation hardness values at load 0,5N that was

achieved compared to basic non-annealed PLA, was 32%. It was apparent from all measurements that the crystallinity change can significantly influence behavior of surface layer on the transition amorphous and crystalline phase.

Annealing of PLA according measured results can be used for modification of surface layer. Properties change can be used by the industry or medical facilities, different degradation time can be used due to different structure.

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LIST OF ABBREVIATIONS

PLA- Poly lactid acid

°C   Celsius degree

A   Indentation surface

AC   Alternating current

Ap   Projected area

A_p Projected contact area

As   Surface area

Bq   Becquerel

c   Geometric constant

C_{IT} Indentation creep

Cp   Correction factor related to the shape of the indenter

DSI   Depth sensing indentation

E*   Complex modulus

E_{IT} Indentation modulus

E_r Reduced modulus

eV   Electro-volt

F   Indentation force

Gy   Gray

H   Hardness

h   Indentation depth

h_1 indentation depth in time T_1

h_2 indentation depth in time T_2

H_A Value of hardness is measured by hardness tester type A

hc   Calculated by the depth of indenter contact with test sample during P_{max}

H_{CH} Berkovich hardness

H_D Value of hardness is measured by hardness tester type D

H_{IT} Indentation hardness

HK   Knoop hardness

HM   Martens hardness

h_{max} Maximum indentation depth

h_p Contact depth

hr   depth intersection

h_s Depth during partially unloading

J   Joule

kg   Kilogram

L   Length is indentation along its long axis

l   Measured height of triangle in indentation

MPa   Mega Pascal

N   Newton

P   Load

PA   Polyamide

PC   Polycarbonate

PE   Polyethylene

PHA   Polyhydroxyalkanoates

PLA   Polylactid acid

P_{max} Maximum loading force

PMMA   Poly(methyl methacrylate)

POM   Polyoxymethylene

PP   Polypropylene

PS   Polystyrene

PTFE   Polytetrafluorethylene

PVA   Polyvinyl acetate

Rad   Radian

R_{IT} Relaxation of indentation

Rpm   Revolutions per minute

S   Contact stiffness

v_i Poisson ration of indented tool

W   Magnitude of the load [kg]

W_{elast} Elastic deformation work of indentation

W_{plast} Plastic deformation work of indentation

W_{total} Total mechanical indentation work

α   Indenter angle

β   Correction factor

η_{IT} Relaxation coefficient

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APPENDICES

EXTENDED ABSTRACT

Cílem diplomové práce bylo měření micromechanických vlastností povrchové vrstvy modi fikovaného Polylactid acid-PLA.

Bio polymery jsou čím dál více využívány ve výrobě díky nedostatku fosilních paliv, průmysl by se měl zaměřit na snížení ceny výroby biopolymerů. Né všechny biopolymery mají však stejné vlastnosti jako polymery z fosilních paliv, takže by pozornost měla být zaměřena i na modifikace těchto polymerů tak aby vlastnosti mohli být pozměněny dle použití.

Modifikace PLA ovlivňuje strukturu a tím jeho užitné vlastnosti. Vzhledem k degradaci PLA hraje důležitou roli při procesech, které vlastní degradaci ovlivňují. Tyto procesy je možné sledovat různými způsoby např. FTIR, DSC, Raman.

Práce popisuje, možnost sledovaní strukturních změn temperovaného PLA pomocí instrumentované zkoušky mikrotvrdosti. Tato metoda umožňuje velmi podrobně popsat mikromechanické vlastnosti testované povrchové vrstvy po temperaci.

Zkušební vzorky byly připraveny technologií vstřikování na vstřikovacím stroji ARBURG ALLROUNDER 470C a poté byly modifikovány temperací o teplotách 90, 100, 110, 120, 130, 140 °C. Změny mikromechanických vlastností povrchové vrstvy temperovaného PLA byly měřeny Instruomentovanou Zkouškou Tvrdosti –DSI. Zkušební vzorky byly měřeny zatěžujícími silami 0,5 N, 1 N, 5 N. Na každém zkušebním tělese bylo provedeno pět měření. Výsledky byly následně zhodnoceny a graficky znázorněny. Pro snadnější orientaci byly použity tzv. bezrozměrné jednotky vyjadřující poměr každého měření ku maximální hodnotě základního (nemodifikovaného) PLA v každém procesu měření.

Nejvyšší hodnoty vtiskové tvrdosti H_{IT} byly naměřeny u PLA temperovaného teplotou 100°C. Rozdíly hodnot aplikovaného zatížení se nejvýrazněji promítly také u PLA temperovaného teplotou 100°C. Nejvyšší nárůst hodnot vtiskové tvrdosti ve srovnání se základním materiálem byl 30% u zatížení 1N. Z výsledků měření je zřejmé že změna krystalinity a velikosti sférolitů ovlivňuje chování povrchové vrstvy na přechodu amorfní a krystalické fáze.

PLA temperované teplotou 100°C mělo nejvyšší hodnoty vtiskového modulu E_{IT}. Také rozdíly hodnot aplikovaného zatížení se nejvýrazněji promítly u PLA temperované tep-

lotou 100°C. Ve srovnání se základním (nemodifikovaným) materiálem byl největší nárůst hodnot vtiskového modulu 16% u zatížení 1N. Změna krystalinity a velikost sférolitů ovlivňuje chování povrchové vrstvy modifikovaného PLA.

Nejvyšší hodnoty vtiskového tečení C_{IT} byly pozorovány u vzorků PLA temperovaných o teplotě 110 a 140°C. Rozdíly hodnot aplikovaného zatížení se nejvýrazněji promítly u PLA temperovaného teplotou 110°C. Ve srovnání se základním (nemodifikovaným) materiálem byl největší nárůst hodnot vtiskového modulu 32% u zatížení 0,5N.