

**UNIVERSITY OF WEST BOHEMIA
FACULTY OF ELECTRICAL ENGINEERING
DEPARTMENT OF MATERIALS AND TECHNOLOGY**

Master's thesis

**The effect of thermal exposure on the properties of
polymer films**

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Jméno a příjmení: **Bc. Jiří KOPŘIVA**
Osobní číslo: **E18N0017P**
Studijní program: **N2612 Elektrotechnika a informatika**
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Zásady pro vypracování

1. Proveďte rešeršní úvod do problematiky termoplastických materiálů.
2. Definujte základní rozdíly mezi PET a PEN polymerními materiály a uveďte konkrétní možnosti jejich využití.
3. Realizujte testovací vzorky pro ověření vlivu dlouhodobého tepelného stárnutí na vlastnosti PET a PEN polymerních materiálů.
4. Stanovte testovací proceduru s vhodnými intervaly pro ověření vlivu tepelné expozice.
5. Proveďte měření dielektrických a mechanických vlastností a výsledky diskutujte.



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1. CARRAHER, Ch. E. a R. B. SEYMOUR. Seymour/Carraher's polymer chemistry. New York: M. Dekker, 2003
2. YASUFUKU, S. Application of poly(ethylene naphthalate) films to electrical and audio-visual uses in Japan. IEEE Electrical Insulation Magazine. 1996, 12(6), 8-14.
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Vedoucí diplomové práce: **Ing. Jaroslav Hornak, Ph.D.**
Katedra materiálů a technologií

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Prof. Ing. Zdeněk Peroutka, Ph.D.
děkan



Doc. Ing. Aleš Hamáček, Ph.D.
vedoucí katedry

Abstrakt

Předkládaná diplomová práce je zaměřena na zjištění vlivu dlouhodobé tepelné expozice na PET a PEN fólie. V první části je proveden krátký úvod do obecné problematiky termoplastických materiálů, jsou představeny stručně fyzikální vlastnosti dielektrické a mechanické a je prezentován krátký přehled o testovacích metodách. Jsou také porovnány PET a PEN filmy z hlediska jejich základních vlastností a uvedeny příklady jejich využití. Dále je pak představena realizace a popis testovaných vzorků a jejich následné kondicionování dlouhodobou tepelnou expozicí. Zdokumentovány jsou také průběhy testů. V poslední části jsou poté předloženy získané výsledky.

Klíčová slova

Termoplast, Polymer, Polyester, PET fólie, PEN fólie, Dlouhodobá tepelná expozice, Dielektrické vlastnosti, Mechanické vlastnosti, Širokopásmová dielektrická spektroskopie, Síla v tahu, Permitivita, Ztrátový činitel

Abstract

This master's thesis presents the study of the effect of long-term thermal exposure on the dielectric and mechanical properties of PET and PEN films. The thesis starts with a brief introduction of polymer materials and a presentation of their dielectric and mechanical properties. Furthermore, possible test methods are briefly introduced. The general properties of PET and PEN films are compared together with the examples of usage. After the introduction, the realization and description of test samples is presented and their conditioning by a long-term thermal exposure is also described. Lastly, the documentation of test runs is presented together with the gained results.

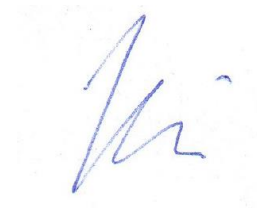
Key words

Thermoplastic, Polymer, Polyester, PET film, PEN film, Long-Term thermal exposure, Dielectric properties, Mechanical properties, Broadband dielectric spectroscopy, Tensile strength, Permittivity, Loss factor

Statement

I therefore declare, that created this Master's thesis on my own, with the help of professional literature and information sources stated in the list that is part of this thesis.

I further declare that all software used in solving this thesis is legal.

A handwritten signature in blue ink, appearing to be 'Jiří', is centered on the page.

signature

In Pilsen 26.5.2021

Bc. Jiří Kopřiva

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I would therefore like to give my sincere thanks to my supervisor Ing. Jaroslav Hornak, Ph.D. for his patience, guidance, professional advices during my work on this thesis and his assistance with samples conditioning and additional test runs during these turbulent times. I would also want to express my sincere thanks to my whole family for everlasting support and help through my whole study.

Content

| | |
|---|-----------|
| CONTENT | 8 |
| INTRODUCTION | 10 |
| LIST OF SYMBOLS AND SHORTCUTS | 11 |
| SHORTCUTS | 11 |
| CHEMICALS | 11 |
| PHYSICAL QUANTITIES AND CONSTANTS | 11 |
| 1 POLYMER MATERIALS - BASICS | 13 |
| 1.1 INTRODUCTION OF POLYMER MATERIALS | 13 |
| 1.2 THE HISTORY OF POLYMERS | 14 |
| 1.3 THE HISTORY OF POLYMERS - TIMELINE | 17 |
| 1.4 TYPES OF POLYMERS | 18 |
| 1.5 PRODUCTION OF POLYMERS | 19 |
| 1.6 GENERAL PROPERTIES OF POLYMERS | 20 |
| 1.7 ADDITIVES | 22 |
| 2 ELECTRICAL PROPERTIES OF POLYMERS IN FREQUENCY RANGE | 25 |
| 2.1 PERMITTIVITY | 25 |
| 2.2 DIELECTRIC LOSSES | 27 |
| 2.3 DIELECTRIC STRENGTH | 28 |
| 2.4 POLARIZABILITY | 28 |
| 3 BROADBAND DIELECTRIC SPECTROSCOPY | 30 |
| 3.1 MEASUREMENT OF PERMITTIVITY VIA BDS | 31 |
| 3.2 FOURIER CORRELATION ANALYSIS | 31 |
| 4 MECHANICAL PROPERTIES OF POLYMERS | 33 |
| 4.1 TENSILE PROPERTIES | 33 |
| 4.2 TENSILE RELAXATION | 35 |
| 4.3 BENDING AND FLEXURE | 36 |
| 5 PET AND PEN MATERIALS | 37 |
| 5.1 INTRODUCTION OF PET AND PEN THERMOPLASTIC POLYESTERS | 37 |
| 5.2 PRODUCTION OF PET AND PEN FILMS | 38 |
| 5.3 COMPARISON OF PET AND PEN FILMS | 38 |
| 5.3.1 <i>Mechanical properties</i> | 39 |
| 5.3.2 <i>Optical properties</i> | 39 |
| 5.3.3 <i>Radiation resistance</i> | 39 |
| 5.3.4 <i>Thermal properties</i> | 40 |
| 5.3.5 <i>Electrical properties</i> | 40 |
| 5.4 USAGE OF PET AND PEN MATERIALS | 41 |
| 5.4.1 <i>Usage of PET material</i> | 41 |
| 5.4.2 <i>Usage of PEN material</i> | 41 |
| 6 SAMPLES PREPARATION AND TEST PROCEDURES | 42 |
| 6.1 BASIC DESCRIPTION OF TEST SAMPLES | 42 |
| TENSILE PROPERTIES | 44 |
| 6.2 | 44 |
| 6.2.1 <i>Shape and dimensions</i> | 44 |
| 6.2.2 <i>Testing procedure</i> | 45 |
| 6.3 DIELECTRIC PROPERTIES | 47 |

| | | |
|----------|--|-----------|
| 6.3.1 | Testing procedure | 48 |
| 7 | RESULTS..... | 50 |
| 7.1 | MECHANICAL TEST RESULTS | 50 |
| 7.2 | ELECTRICAL PROPERTIES IN FREQUENCY RANGE – RESULTS | 52 |
| | CONCLUSION..... | 55 |
| | BIBLIOGRAPHY AND INFORMATION SOURCES..... | 56 |
| | ATTACHMENTS..... | 1 |

Introduction

The presented master's thesis is focused on the study of an effect of a long-term thermal exposure on the dielectric and mechanical properties of polymer films.

The text can be divided into four main parts. The first part introduces the polymer materials in general. The history and evolution of polymer materials is discussed, their basic properties and possible modifications are also presented. Their dielectric and mechanical properties are also presented together with possible testing methods. The second part consist of a closer introduction of a PET and PEN film materials, comparison of their basic properties and presentation of usage examples. The third part documents the realization and conditioning of the test samples by a long-term thermal exposure. Preliminary test, which purpose was to find out the ideal temperature for conditioning, is also presented. This is followed by the documentation of test runs. The last part then presents the achieved results and evaluate them, compare the results gained by tension in pull endurance test and the broadband dielectric spectroscopy for PET and PEN films.

List of symbols and shortcuts

Shortcuts

| | |
|------------|-----------------------------------|
| A.D. | Anno Domini |
| AC..... | Alternating current |
| BDS | Broadband dielectric spectroscopy |
| DC..... | Direct current |
| DNA | Deoxyribonucleic acid |
| MEMS | Microelectromechanical systems |
| TFT | Thin-film transistor |

Chemicals

| | |
|--------------------------------------|----------------------------|
| Al | Aluminum |
| Al ₂ O ₃ | Aluminum oxide |
| CH ₂ | Methylene |
| PEN..... | Polyethylene Naphthalate |
| PET | Polyethylene Terephthalate |
| PF..... | Phenol formaldehyde |
| ZnO..... | Zinc oxide |

Physical quantities and constants

| | |
|--|---------------------------------------|
| A, B..... | Material constants – thermal aging |
| A ₀ | Cross-section area (mm ²) |
| b, b ₁ , b ₂ | Width (mm) |
| C | Capacitance (F) |
| F..... | Force (N) |
| <i>f</i> | Frequency (Hz) |
| h | Thickness (mm) |
| I..... | Current (A) |
| k | Polarizability (-) |
| l, l ₀ , l ₃ | Length (mm) |
| P..... | Performance (W) |
| Q..... | Electric charge (C) |
| r, r ₂ , r ₃ | Radius (°) |
| T..... | Temperature (°C) |

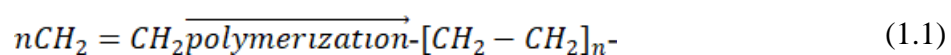
| | |
|-------------------------------|---|
| T_g | Transition temperature (°C) |
| $\text{tg}\delta$ | Dielectric loss (-) |
| T_m | Melting temperature (°C) |
| V | Voltage (V) |
| δ | Tension in pull (MPa) |
| ε | elongation (%) - in mechanical properties |
| ε | Permittivity (F/m) - in electric properties |
| ε_0 | Permittivity of vacuum (F/m) |
| ε_r | Relative permittivity (-) |
| $\varepsilon'(\omega)$ | Real part of relative permittivity (-) |
| $\varepsilon''(\omega)$ | Imaginary part of relative permittivity (-) |
| τ | Service life of insulation (h) |
| v | Temperature (°C) |
| Φ | Phase shift (°) |
| ω | Angular velocity (rad/s) |

1 Polymer materials - basics

Plastics are widely used materials in today world, encompassing even the electrical engineering branch of the industry. These materials are used in every sector of electrical engineering, from high voltage applications like energy transmission or creation of insulation layer for electric motors, to small applications like microphone, in a form of a membrane, or simply wire insulation [1-5].

1.1 Introduction of polymer materials

Term „plastic“ refers to materials created from polymers enriched with additives via many different fabrication methods. These methods can be various types of molding or extrusion [1]. Polymers can also be referred to as plastic resins and their name is derived from Greek words of *polys* and *meros*, meaning “many” and “parts” and was firstly introduced by Jöns Jakob Berzelius, a Swedish chemist [6]. Nature of the polymer can be organic (for example various proteins or even DNA) [1], synthetic (like the polyethylene terephthalate, shortly PET) [1], to even hybrid inorganic-organic polymers consisting of inorganic base enriched with organic components [1]. All of them share the same basic structure, because they are all large molecular compound materials consisting of repeating monomers. As an example, one of the most favored polymer is polyethylene, composed of recurring monomer, which is ethylene, bond together via covalent bonds [2]. Every polymer consist of very long chains formed from the monomers, with varying lengths and chaotic distribution. This characteristics is referred to as „a bowl of worms or spaghetti“ [1]. This chaotic distribution also causes, that the stiffness of the bulk is much lower than the theoretical stiffness of molecules. For example, the stiffness of polyethylene as bulk is about 1000 (MPa), while the theoretical stiffness of its molecule can reach 300 000 (MPa). The length of monomer chains are defined by the manufacturing method used in creation of the material and conditions during its´ creation like temperature, pressure or the type of used catalyst. Below is an example chemical formula, visualizing the process of polymerization of ethylene (CH₂). The degree of polymerization (*n*) refers to the amount of recurring monomer units in the chain and thus, it shows its´ length. The degree of polymerization of the polyethylene is usually above 10,000. [1][2][3][6]



Among the main reasons standing behind the success of plastic materials is their relatively low melting point, which compared to glass or metals mean much more energy saving and thus more effective processing. Also, the plastic can be much easier to form into complex shapes thanks to for example injection molding. Plastic materials are actually so easy to process, that even parts can be directly printed from it without any complications [7]. Due to their nature some of them are excellent electrical insulators and also, depending on their structure, those materials can serve as an excellent thermal insulation. They can also be very resistant to various chemicals or biological (such as bacterial or fungi influence) [8]. Polymers can also be produced with wide range of flexibility and toughness. Least, they can be fabricated with a wide range of possible surface finish, even create the illusion of metals. This for example can be seen on mobile devices, as some mobile companies manufacture their devices with an aluminum chassis, they also generally offer a cheaper variant from plastic, which is nearly identical on the first look to the luxury metal variant. [5][7][8]

1.2 The History of polymers

Plastics did not have such a large impact as the entire age to be named after them, such as stone age or bronze age, even though, they are a very important part of today industry. The history is very well described in a book [4]. The history of plastic materials starts with the emergence of naturally made materials in ancient records. Indeed, the first written records of what is supposed to be an ancient predecessor of today plastics, can be found in the book of Genesis. There, it is speculated, that process of using a bullrushes together with slime and pitch in Chapter 2 describes the actual creation of one of first types of plastic boat. Also, the electron got its name thanks to the fossil resin named amber, which is called *elektron* in Greek. This was caused by the last of the series of 37 books called *Natural History*, written in the era of ancient Rome by Pliny the Elder (c. A.D. 23-79). In this book, it is noticed the ability of amber to attract dust. Another historical mention about the usage of previously mentioned lac is from the scientific mission to India, dated in 1596 and led by the John Huyglen von Linschoeten. This written mention describes the usage of the substance named shellac, which is still used to this day, albeit under the name of Indian turney. [4]

In the record, it is stated the following:

„Thence they dresse their besteds withall, that is to say, in turning of the woode, they take a peece of Lac of what colour they will, and as they turne it when it commeth to his fashion they spread the Lac upon the whole peece of woode which presently, with the heat of the turning (melteth the waxe) so that it entreteth into the crestes and cleaveth unto it, about the thickness of a mans naile: then they burnish it (over) with a broad straw or dry rushes so (cunningly) that all the woode is covered withall, and it shineth like glasse, most pleasant to behold, and continueth as long as the woode being well looked unto: in this sort they cover all kind of household stufte in India, as Bedsteddes, Chaires, stooles, etc....“ [4]

One of the first materials to be used in electrical engineering industry is so called gutta percha. This natural resin was used during the 19th century as a cable insulation material and was pushed out in favor of synthetic materials around the year of 1940. It was introduced to the world by a gardener and traveler named John Tradescant (1608-1662) [4]. The first thermosetting plastic was a rubber, discovered among the natives of Central America by the sailors of Columbus in 1492. The discovered rubber was obtained from *Hevea* tree and it is said, that it was used to create a rubbery ball used by natives during their sport activities. This rubber was then experimented with and in a year 1839 it was discovered, that when heated with sulfur, the material retains its elasticity and is reasonably resistant to solvents. Further experiments with different amount of sulfur used then led to the invention of so-called ebonite. This discovery, with patent created in 1851 by Nelson Goodyear, is considered to be so important to the history of plastic materials, as it is called a milestone in the history of rubber industry. [4][5]

The establishment of polyethylene was during the first decade after the second war. At that time, this material, together with others like polystyrene, was not widely used as its usage was mostly focused on special and expensive applications. However, the production slowly increased to the point, it was produced *en masse* at enormous quantities and started to not only being competitive to other established materials, but even surpassing them to the point of beginning to replace them. This boon of polyethylene usage also led to some instances, where it was not the most suitable material and thus did some damage to the reputation. [4]

Fortunately, these „experiments“ with boundaries of the possible usage became more and more understood by time and although, for example, the wood rot, metal rust and glass easily shatter, those materials are being still used and still retain an important place even in today industry. The high density polyethylene started to emerge on the market in the 1950s, and were produced by the Ziegler [4] or Phillips [4] processes. Those materials then registered slight decline of usage as the new material of polypropylene [4].

Other interesting thing in the evolution of plastic is the raw material used for it's manufacture. First raw materials took form of a plant matter, which was the cellulose [4]. From this raw material was produced for example nylon. There were even experiments with soy beans by Henry Ford and of course natural rubber was also used. Polyethylene was firstly being obtained from sugar cane via molasses, ethyl alcohol and ethylene. This process is still being used today, albeit rarely. There were even tests with the usage of animal matter and their products were for example blood albumin or shellac. [4]

Commonly used raw material in the Europe during the first half of 20th century was coal [4]. Coal can be taken apart by the destructive process and this process yield four products, which are ammonia, coal gas, coal tar and coke. Coal tar serves as the source of aromatic chemical like naphthalene. All other products of course also have their own uses as, for example, coke can be used for acetylene production together with calcium oxide and water. Another material, which initiated the boon of the plastic industry is the petroleum. The first petrochemical industry emerged after the World War I although, it was mostly focused on the production of solvents of olefins, but this was merely a waste product during the manufacture of gasoline and other such substances. By the nearing end of the second war, the petrochemical industry became to develop and yielded products such as ethylene glycol or ethylene oxide. Over time, the petroleum pushed out coal as the prominent raw material for the production of polyethylene. [4]

Polymer materials can also being sorted by their order of emergence in the industry, so called „generations“. The first materials to emerge, and thus being sorted as *the first generation*, were the polystyrene, low-density polyethylene or the first synthetic paints. The high-density polyethylene emerged in the *second generation* between yeas of 1950 and 1965. In this generation also emerged polyurethanes, epoxy resins or aromatic polyesters to mention few. The *third generation* then saw not only new materials, which chemical structure was far more complex, leading to higher stability (both thermal and

chemical) and also higher stiffness. The time of the *third generation* also encompasses large improvements of thermoplastic polyethylene. The last *fourth generation*, which encompasses materials developed from the '90s till today saw the introduction of far more sophisticated fabrication technology, which enabled the creation of materials encompassing nanoparticles called nanocomposites, much more defined or even specifically designed and shaped structure or even so called „green polymers“ fabricated from alternative raw materials to fossil fuel. [5]

1.3 The History of polymers - timeline

The historic timeline is well-described in a book [9].

1835 – Liebig and Regnault reported the existence of vinyl chloride

1862 – Parkes discovers first plastic material based on nitrocellulose

1866 – Hyatt creates first man-made plastic material based on nitrocellulose

1884 – Tollens describes the use of PF in polycondensation in creation of amino resins and amino plastics

1897 – First production of galalith in Germany by reaction of casein (milk protein) and formaldehyde

1898 – Einhorn reported on the formation of polycarbonates

1900 – Usage of first thermoplastic celluloid for movie film

1907 – Bakeland created first thermoset polymer (phenol-formaldehyde)

1909-1910 – Commercialization of Bakelite

1912-1916 – Klatt discovered vinyl-chloride photo-polymerization

1918 – John patented the use of PF in polycondensation in creation of amino resins and amino plastics

1926 – Ostramislenski patented flexible film cast from a solution of PVC and plasticizer

1933 – Ellis's discovery of unsaturated polyesters

1933 – Gibson and Fawcett accidentally discovered high-pressure polymerization of ethylene

1935 – Carothers discovered nylon66 as fiber-forming polymer

1936 – Schlack discovered nylon6

1938 – The breakthrough development of fluoropolymers through synthesis of poly(tetrafluoroethylene)

1941 – Whinfield and Dickson discovered PET

1950s – Development of basic technology for production of polymer foams

1954 – Ziegler Natta discovery of crystalline polypropylene

1955 – First mass production of PET

1957 – Commercialization of polypropylene

1960s – Development of vinyl ester resins

1965 – Introduction of Polysulfane

1973 – DuPont started to produce Kevlar

1980s – Start of continuous development of high-performance polymers such as polyamide 4-6

1.4 Types of polymers

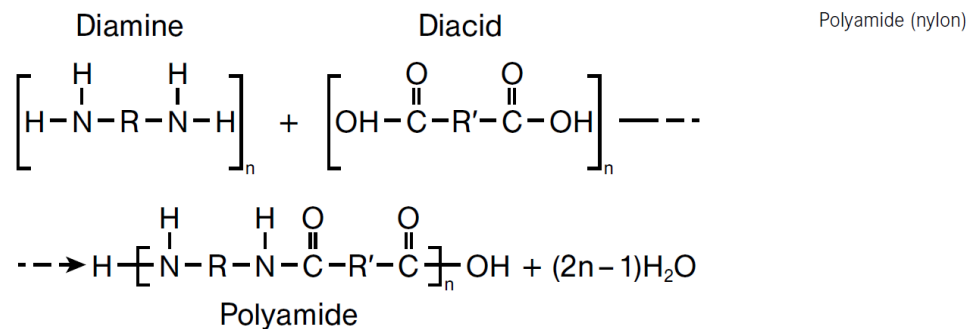
Plastic materials can be divided into three main types, which are thermoplastics [1], thermosets [1] and elastomers [1]. For the total basics, thermoplastics are able to be heated to certain temperature and molded thanks to the ability of the molecules to „flow“ in a material during a high temperature [3]. After this, this type of polymer is able to solidify again, when it returns to lower temperature because the motion of the long molecules is restricted again. This process of heating, making the material pliable to molding and then cooling down, thus solidify the material, can be repeated and exists thanks to the aforementioned inner structure of the material. On the other hand, thermosets and elastomers, which are pliable and relatively soft in normal circumstances, are invariably hardened by, for example, heating up, exposing to a specific form of radiation or pressure. This inevitable hardening of thermosets is caused by chemical curing process [3], and for elastomers, this process is called vulcanization [3]. During the curing, the macromolecule chains create a network via crosslinking with each other. This high concentration of crosslinking then prevents any molecules to „flow“ after re-heating the material. Other difference can be shown in its inner structure. [1][3]

While thermosets are characterized by the cross-linking in their structure, thermoplastic material are characterized by their crystallinity. Thermoplastic materials can be further divided into amorphous or semicrystalline, although, these materials are considered to be so similar, that they are both called just „thermoplastic“ [1][3]. The degree of crystallinity in amorphous materials is 0 % and so, they are naturally transparent materials, as these materials lack the crystalline structures due to their chaotic arrangement, which would obstruct the passing light. The amorphous thermoplastic materials solidify below its glass transition temperature T_g (°C) [1][3]. Semicrystalline material can have various degrees of crystallinity, although it never reaches 100 % [1]. This occurs, because macromolecules tent to arrange themselves in a pattern below their melting temperature T_m (°C) although not all molecules do so, which creates amorphous regions in the material. These amorphous regions solidify at a glass transition temperature T_g . Due to its effect, it is nearly impossible to determine the exact melting point for the testing sample as the actual melting point vary, although in very small degree, by each sample. The semicrystalline materials' glass transition temperature T_g is located below the freezing point [1][3].

1.5 Production of polymers

The macromolecular structure of polymers can be created via both synthetic and organic process [3]. Among the organic polymer materials, which can be found naturally, belongs for example silk, amber or wood. Naturally occurring inorganic materials are then glass or quartz. For the creation of synthetic polymers, there are two methods used. Those methods are addition polymerization and condensation polymerization. Polymers can also be divided to commodity and engineering plastics. Commodity plastics have high volume and low cost, and their typical examples are polyethylene, polypropylene or poly(vinyl chloride)[9]. The examples for engineering plastics, which are characterized by high cost and low volume, are polycarbonate, polyimide or poly(etheretherketone)[9]. [3][9]

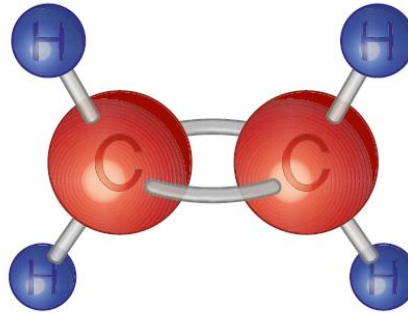
The condensation polymerization is induced by mixing two components, which end-groups can react with each other. As the end-groups reacts, the macromolecular chain is created and the end-groups forms a by-product. This can be shown for example on the creation of nylon (polyamide). In this case, a diamine and diacid react, creating the aforementioned polyamide with the water as a by-product. [3]



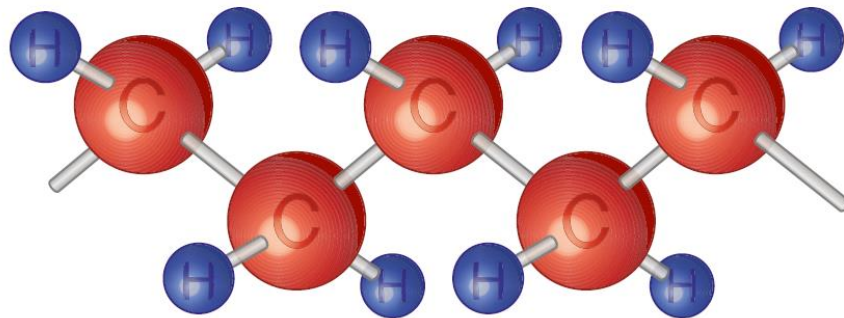
Scheme 1.2 Polyamide creation via condensation polymerization "taken from [3]"

The other method mentioned is addition polymerization. This method takes advantage of the double bond occurring between two carbon atoms. This double bond is broken, allowing the carbon atom to link to the neighboring carbon atom and thus creating a long chain. The example can be shown on the creation of polyethylene from ethylene monomers. Thermoplastics materials are commonly created this way. [3]

Ethylene



Polyethylene



Scheme 1.3 Schematics of Ethylene monomer and a Polyethylene long chain "taken from [3]"

1.6 General properties of polymers

One of the general characteristics of the polymer, which determines its properties, is the molecular weight [3]. The molecular weight of a polymeric material cannot be precisely determined as the main reason for this is the various lengths of monomer chains in a bulk of the material. Unfortunately, the properties of the material are linked strongly with the molecular weight, which depends on the length of the chain, and thus it is needed an approximation. For this reason, the molecular weight is usually shown as an average determined by the degree of polymerization [3]. In the figure below (*Figure 1.4*), it is shown how the molecular weight affect the mechanical property of the polymer material. [3]

This molecular weight and degree of polymerization affect the properties of the bulk as for example in polystyrene. If the degree of polymerization of this material is 1000, the material is brittle and stiff at room temperature, while for the degree of polymerization of 10, the material very soft at the same temperature [3].

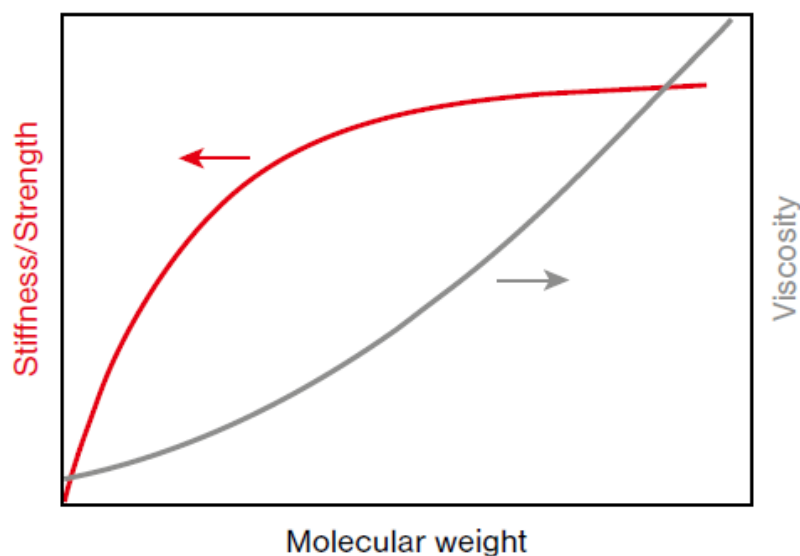


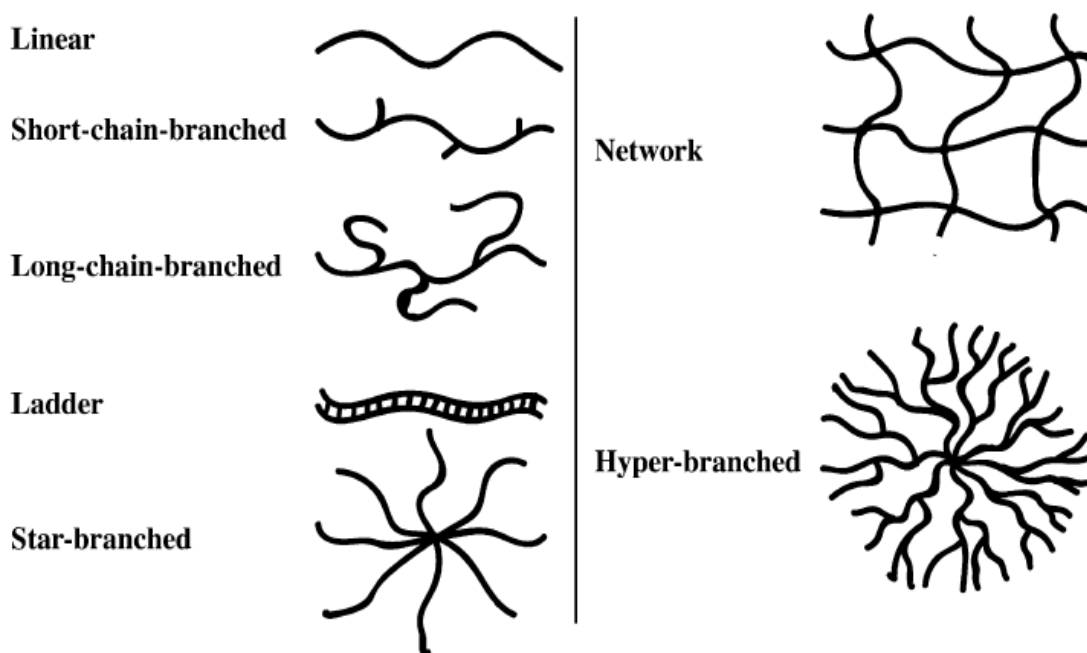
Figure 1.4 Mechanical properties according to the molecular weight “taken from [3]”

Besides the molecular weight is also important factor the molar mass. The size of the polymers, which form the polymer material is quite large and it affects the location of the melting point. Substances with low molar mass have their melting point increased with the increase of their molar mass. On the other hand, for polymers with their already high molar mass of molecules, the melting point of the polymers is nearing to become a constant. Unfortunately, this does not mean any specific set melting point as there is no available fabrication method which would yield a material with a single size of its' molecules. [5]

Because the decrease of the range size of molecules is quite important for further development and for refining the properties of the materials, there is an intention to restrict the size of the molecules [5]. This also creates the need for the development of methods for molar mass determination. To mention few, some of the methods experimentally used are size exclusion chromatography, ultracentrifugation or light scattering. [5]

This effect of stabilization with increase of molar mass is also similar with other properties, such as Young's modulus or fracture toughness. The reach of these properties is mostly found around the molar mass of 20 kg mol^{-1} and above [5]. This unfortunately mean, that the polymer materials with high molar mass are more complicated to work with and process, although with much better results in mechanical properties of the final product. [5]

Another factor influencing the properties of the material, for example crystallinity or final structure, is possible branching of the monomer chains [3]. The branching is formed during polymerization, because of irregularities which occur during this process. To explain it briefly, the length and density of the branches determines the crystallinity and thus the density of the material, as higher number of branches and their longer structure results in material with lower degree of density, because its degree of crystallinity is also lower. The branching can also occur on the branches themselves. To mention an example, the degree of crystallinity of polyethylene depends mostly on branching and a cooling rate of the produced material. Different types of possible structures are shown below (*Scheme 1.5*). [3]



Scheme 1.5 Schematics of possible structures formed from molecular chains "taken from [5]"

1.7 Additives

The properties of polymers are often enhanced by mixing in additives, as pure polymers are seldomly sold. The additives can alter, for example, color of the material, enhance its mechanical properties or can make the processing itself of the polymer easier.[3]

As most polymer materials are flammable, there is sometimes need to decrease the chances of the ignition or slowing the spread of flame of already ignited materials, reduction of the thermal energy released, spread of the flame or to reduce the production of dangerous by-products. The thermal degradation can be separated into 4 phases, which are heat up, pyrolysis, ignition and a spread of the flame [10]. The additives achieve this by varying ways of influence. The process of flame retardation can be further divided into physical and chemical. Between physical then belongs for example influence of cooling or non-flammable substances, followed by creation of barriers on the surface or inside the material. Amongst the additives with physical effect can be found for example clay, additives on the hydroxide basis (such as aluminiumtrihydrate or magnesiumdihydrate) [10]. Chemical retarders work via activation as free radical capture and the initiation of chain-reactions and networking. Chemical retarders can be divided on the basis of their composition such as halogen retarders (brominated and chlorinated substances), phosphorus based retarders, silicone retarders, nitrogen based retarders or inorganic additives. [3][10]

Another problem, which the additives are able to tackle, is a charge generation. Because of the overall low electrical conductivity of polymers, the charge is easily built on the surface. This charge depends on the charge generation and charge decay. Both of these factors can be improved by antistatic agents. The charge generation rate can be reduced by the reduced intimacy of the surface, while the charge decay can be improved by surface conductivity. Because of this, there is use of ionizable additives as antistatic agent [3]. This additive allows the charge to migrate to the surface more easily, where bridges in the surrounding atmosphere can be created thanks to the moisture. For this purpose, nitrogen compounds are being used, as for example polyhydric alcohols or long-chain amines. [3]

Next types of additives to mention are fillers. Fillers usually differ by a great margin in its' structure, properties and chemical composition from polymers and their purpose is to alter the physical properties of polymers. Even chemical properties can be altered, as there are possible interactions of both materials in the place of their contact. The important properties in a selection of the right filler for specific application. Among the most important properties then belong mechanic, electric and optic properties. In addition, if there are more fillers than just one, the possible chemical interaction between the fillers also has to be considered. Fillers can be on inorganic or organic basis [10]. For the

inorganic fillers can be used various minerals, while organic can be cellulose-based. Next important factor is the shape of the added filler material. From nanofibers, larger fibers for more rigid materials or filler particles. The shape of filler particles can be diverse and can take shape of a wide variety of geometric shapes. Composites are divided to low performance composites and high performance composites [3]. In low performance composites, the size of the reinforcement is so small, it can be dispersed into the matrix. Those materials are then processed the same way as unmodified material. On the other hand, high performance composites are those, which are placed into the polymer, for example, in the form of unidimensional glass fibers. Those high performance composites reinforcement per volume usually reaches 50 (%) to 80 (%) [3]. The most common material to use as a filler is a glass fiber, but wood fiber is also available for use. When adding the filler, it is needed the usage of coupling agents such as titanates to reinforce the bond of the material and the filler. [3][10]

Fillers can also be used to reduce the amount of material needed to make a product. Those fillers are called extenders. This is mostly to reduce the cost of the produced part. For these purposes, for example silica flour, wood flour, clay or calcium carbonate are used. Those polymers, which are most usually used for this application, are also commonly characterized by lower toughness when the extenders are not added. The amalgam of a polymer and filler is called a composite. [3]

All the previously mentioned additives are used to enhance the properties of the final product, so the next types of additives to cover are the ones used to enhance the properties of the polymer during its' processing. Among those additives belongs plasticizers. Plasticizers, or also sometimes called solvents, are sometimes being mixed into a polymer to change its' properties during their processing by a great margin. Their effect on the polymer is similar to heating and thus raising the temperature of the material. This lowers the viscosity of the material and allows it to be processed without degrading the material, as for example cellulose nitride thermally degrades. Other use of plasticizers is to change the mechanical properties of the polymer material, such as stiffness, toughness or strength. [3]

Next types of additives are stabilizers. Stabilizers are important in that, they slow down, for example, the thermal degradation or degradation caused by UV of the polymer [3]. The thermal degradation occurs, when the polymer is exposed to the oxygen and heat. This causes the oxygen to react with free radicals produced by the heat and thus form carbonyl compounds, which can be observed as a yellow or brown discoloration in the final product. This degradation cannot be fully eliminated, but can be slowed down by adding peroxide or antioxidant decomposers. When the stabilizer is fully consumed, the polymer is no longer protected. [3]

Last type of the main additives left to mention are the blowing agents. These are used during the creation of expanded plastics, also called cellular polymers. These cells created can be interconnected „open cells“ or completely enclosed „closed cells“. Simply put, the main reason is to create a foam material. Those foam materials created from polymers can have a density between $1,6 \text{ kg/m}^3$ and 960 kg/m^3 . The usage for such foams is sound or thermal insulation, they can be used to absorb and reduce mechanical vibrations or they can simply be used because of their high strength to weight ratio. Those foams can be created by various mechanical or chemical ways, the simplest way is whipping gasses into the polymer by mechanical means, thus creating bubbles in the material. [3]

2 Electrical properties of polymers in frequency range

2.1 Permittivity

The dielectric behavior of any material is not a set parameter, but depends on many properties and conditions. To name few, there is a dependence on voltage level, pressure, frequency of applied voltage and temperature. Amongst the most important properties of dielectric materials then belongs the conductivity and the current (both AC and DC), dielectric constant defined by the inductive capacity, electric breakdown strength and dielectric loss. Those properties and behavior are studied mostly by applying an electric field, which creates an electric charge or polarization current running through the material. The polarization current is dependable on the size of the electric charge applied and the physical dimensions of the tested sample. Thus, if there is a wish to get the permittivity ϵ , it is first needed to define the capacitance C of the material. [2]

$$\varepsilon = C/C_0 = (Q/U)/C_0 \quad (2.1)$$

The capacitance C represents the measured capacity of the condenser with the dielectric material between its plates in a vacuum, while C_0 is the capacitance of an empty condenser. The charge Q is divided by the voltage U and thus the capacitance C is obtained. This is to eliminate the confusion, which would occur due to the dependence of the capacitance on the sample size and applied voltage as mentioned above. [2]

The permittivity above represents a relative permittivity which is more commonly written as ε_r (-). To get the absolute permittivity, it is needed for the ε_r to be multiplied by a constant vacuum permittivity ε_0 (F/m), which value is $8,854 \times 10^{-12}$ (F/m). [11]

$$\varepsilon = \varepsilon_r \cdot \varepsilon_0 \quad (2.2)$$

In case of alternating electric field, the complex relative permittivity is introduced. [11]

$$\varepsilon(j\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \quad (2.3)$$

Where: $\varepsilon'(\omega)$ is the real part and represents the inherent relative permittivity

$\varepsilon''(\omega)$ is the imaginary part which represents the dielectric losses

The relation between dielectric losses $\operatorname{tg} \delta$ and permittivity is described below. [11]

$$\operatorname{tg} \delta = \varepsilon''(\omega)/\varepsilon'(\omega) \quad (2.4)$$

2.2 Dielectric losses

Dielectric losses can be found in any type of dielectric material. These losses are generally a sum of conductive, polarization and ion types of losses. The most important characteristics affecting the appearance of these losses are the material's structure, its chemical composition and impurities located in the material. For example, some organic polymers can have mostly minimal dielectric losses, as the only type of loss contributing to the sum is the conductive type. The main feature for these materials is thus a loss factor $\operatorname{tg} \delta$ nearing a zero value. By knowing the loss factor, it can be made a general assumption about the quality of the insulation material. If the loss factor is smaller than 10^{-3} it can be assumed, that the insulation is good [11]. Otherwise, if the loss factor is above 10^{-2} the insulation material is generally bad [11]. Interesting fact is, that polar macromolecular materials (both organic and synthetic) have very similar behavior regarding dielectric losses to the polar, highly liquid dielectric materials. The most prominent for this type of materials are polarization and conductive losses. The loss factor $\operatorname{tg} \delta$ is also dependent on the frequency of the electric field, as is shown below. [11]

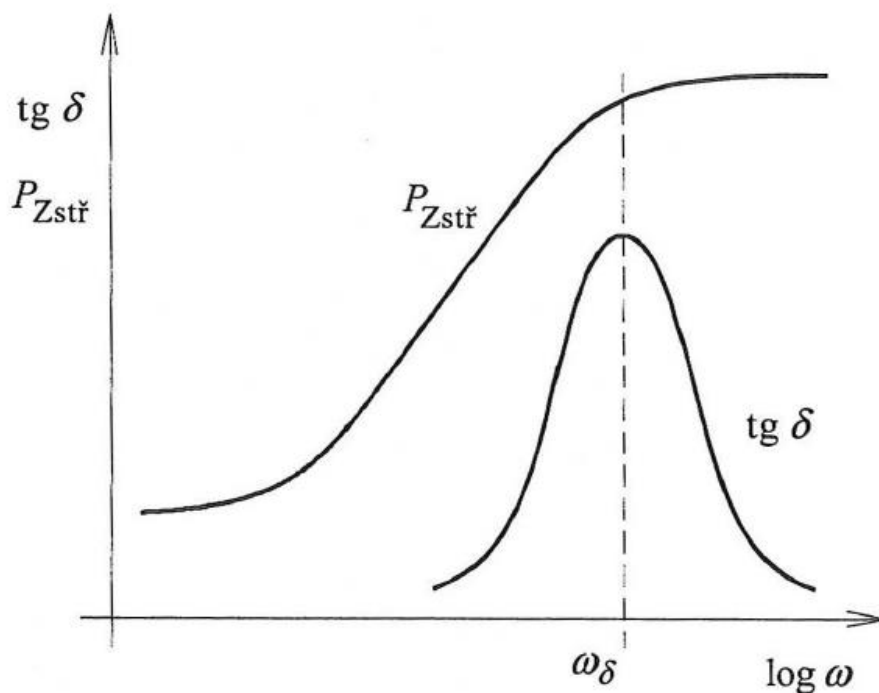


Figure 2.5 Dielectric loss factor's dependence on frequency during constant performance P "taken from [11]"

2.3 Dielectric strength

Dielectric strength is perhaps the most important factor for any dielectric material, as it directly affects its' main function, which is to separate two parts with different electric potential, generally active and grounded part. If the system is badly designed and significant amount of an electric charge, the insulation can be irreversibly damaged and the electric current may occur. In case of solid materials, this event is being referred to as an electric breakthrough. The height of voltage, during which the electric breakthrough occurs is marked as U_P (kV). Other factor affecting the dielectrics strength E_P (kV) is the thickness of insulation d (mm) and other factors such as temperature, pressure, humidity and impurities of the insulation. [12]

$$E_P = U_P/d \quad (2.6)$$

2.4 Polarizability

The next dielectric characteristic, which is related with the permittivity, is polarizability. The polarization of the dielectric occurs spontaneously, or when the material is influenced by the DC or AC electric field. The polarization defines the moment of the molecules induced by the applied electric field, the moment itself defined by the intensity of the field, resulting in the alignment of the molecules according to the direction of the electric field. This is also closely bound with the conductivity, which is defined as a movement of certain amount of ions per unit volume and average velocity of said ions. The movement of ions occurs in the direction of the electric field. The dipoles are basically bound charged particles and by their rotation and displacement occur the said movement of ions, although the conductivity is, by any means, not as in conductive materials. [2][11]

To define the polarizability k , it is needed to know, that two different types of charging current occur during the condenser being charged. Those two are absorptive slow and rapid forming nearly instant polarizations. The instant polarization occurs, when electric field with frequencies over 10^{10} Hz are reached and the change is so fast, that it cannot be observed, until the frequency lowers to correspond with the visible or UV spectrum of light.

The total polarization is thus the sum of both types. The time for the effect to form or dissipate back into its original state after removing from the electric field is called relaxation time. The polarizability is related to the permittivity via a below shown formula. [2]

$$k = \frac{3(\epsilon - 1)}{4\pi(\epsilon - 2)} \quad (2.7)$$

Interesting factor is, that the contribution to the polarizability constant k at high frequencies seem to be only electronic (E) in nature, while the values obtained during low frequencies and DC measurements are a sum of electronic (E), atomic (A), dipole (P), and interfacial (I). This is shown in the following figure (Figure 2.1). [2]

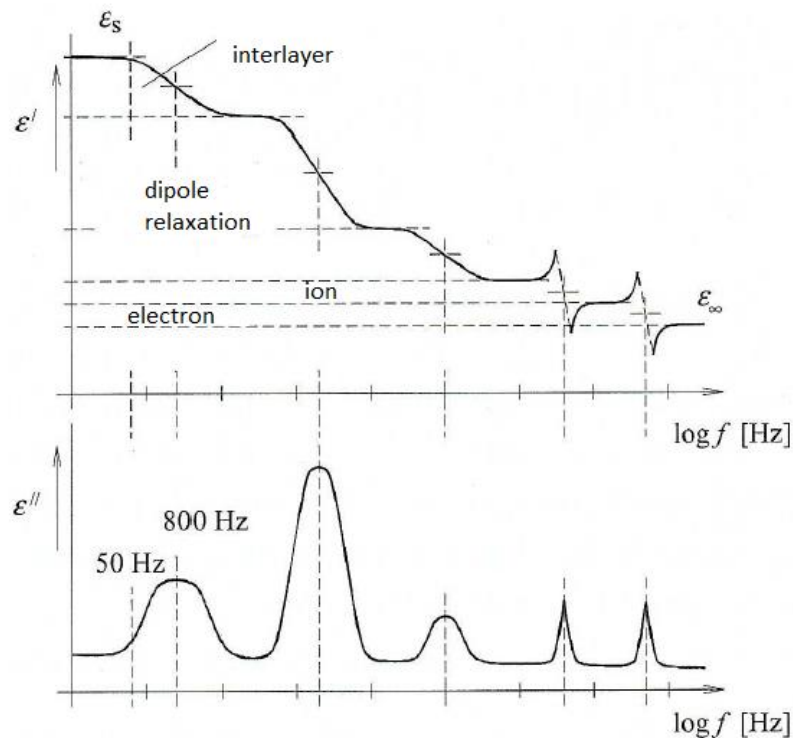


Figure 2.8 Contributions to polarizability in regard to the frequency of electric field "taken from [11]"

In addition to the electronic polarization, this property is dependent on the atomic bonds. This means, that the values measured for small molecules can be applied to the polymeric materials appropriately. However, the polymeric nature of the material can cause an electric conductance of electric charge by the resonance of the whole chain and thus do not allow this application. [2]

To briefly explain the other polarization contributions, let's start with the dipole (P), which can be divided to the major and minor dipole contributions. The mayor dipole contribution is naturally occurring, as those permanent dipoles in molecules tend to align themselves according to the electric field with their axes. The minor dipole contributions then depends on factors, like size and mobility of the unit and both physical and chemical nature of the environment. This type of polarization is an absorptive type. [2]

The atomic (A) polarization occurs due to the natural motion of atoms in a molecule. This is due to the vibrations caused by the perturbation effect of the applied field of vibrating atoms, because atoms and ions have a specific resonance frequency located in the infrared region. Simply put, it is due to the natural movement of atoms caused by the temperature. This contribution is nearly non-existent in organic polymers, which are nonpolar. Atomic polarization is classified as instantaneous. [2]

The previously mentioned types of polarization are the major types found in homogenous materials. The interfacial (I) polarization contribution encompasses different types of this effect caused by the heterogeneity of the material. It can be caused by additives in a material or the natural electrical heterogeneity as is for example in a paper material. [2]

3 Broadband dielectric spectroscopy

Broadband dielectric spectroscopy is a very versatile tool for study of dynamics of polymeric systems, as it can cover a wide range of frequencies from 10^{-3} Hz to 10^9 Hz and this range can be even widened [13]. The basics for this method were laid by Clausius, Mossoti, Maxwell, Kirkwood, Wood and Debbey by describing the behavior of dielectric material in a non-stationary electric field [14]. The BDS allows for a measurement of the complex permittivity of the materials by a system, which combines advantages of Fourier correlation analysis, dielectric converters and impedance analysis, as these devices include direct digital synthesizer generator, direct V-I converter, dielectric converter and two precise sine wave correlators. It evaluates the amplitudes of an electric current I_0 (A), voltage U_0 (V) and their phase shift Φ (°). Even ultralow capacities, such as 10^{-15} (F) can be measured by this method, and exceptionally high-resolution dielectric analyzers are commercially available from a Novocontrol company. [13][14][15]

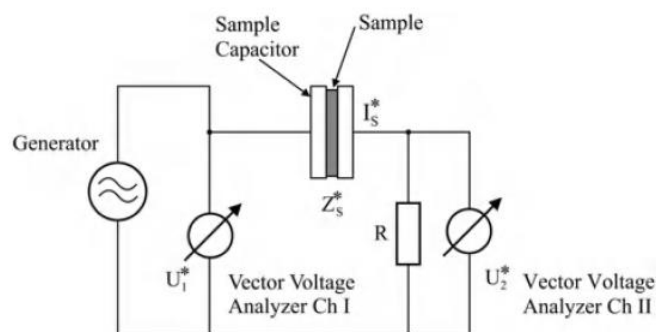
3.1 Measurement of permittivity via BDS

The complex permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - j \varepsilon''(\omega)$ is good to be measured in a very broad frequency range, as through this can be obtained the most relevant results. The frequency can span from to 10^{-6} (Hz) to up to 10^{12} (Hz) [15]. For this large range, a combination of several different measuring methods have to be used. For up to 10^7 can be used the lumped circuit method. In this method, the sample is treated as a parallel or serial circuit of an ideal capacitor and an ohmic resistor [15]. However, with increasing frequency is becoming far more important the shape of the capacitor and also the interferences, such as parasitic impedances are being caused by contacts, cables and such. The mentioned interference starts to become a problem roughly above 100 (kHz) [15]. For higher frequencies (10^7 to 10^{11} Hz) are used so called distributed circuits methods. Through the range of 10^{-6} to 10^{10} (Hz) can also be deduced the $\varepsilon(\omega)$ from time dependent function $\varepsilon(t)$. This function is related to the $\varepsilon^*(\omega)$ via a Fourier transformation shown below. [15]

$$\varepsilon(\omega) - \varepsilon_{\infty} = \int_{-\infty}^{\infty} \varepsilon(t) e^{-i\omega t} dt \quad (3.1)$$

3.2 Fourier correlation analysis

During a Fourier correlation analysis is typically applied a sine wave of a voltage amplitude of $U_1(t)$ with a frequency of $\omega/2\pi$ to the tested sample by the generator. The generator will cover a range of 10^{-6} to 10^7 (Hz). The resistor R then converts the current of the sample $I(t)$ into a voltage $U_2(t)$. The gained data are then analyzed and a complex impedance of the sample Z is calculated. The basic scheme is shown below. [15]



Scheme 3.2 Fourier correlation analyzer "taken from [15]"

The abovementioned setup is seldom sufficient, because the resistor R brings several limitations to the setup, and thus a dielectric converter is used to enhance the Fourier correlation analysis by converting the sample current to $U_2(t)$. This dielectric converter uses a broadband electrometer amplifier with a variable gain. This is because the dielectric measurements require a huge impedance range. This range is usually about 13 orders of magnitude for a range of frequencies of 10^{-3} to 10^7 (Hz). [15]

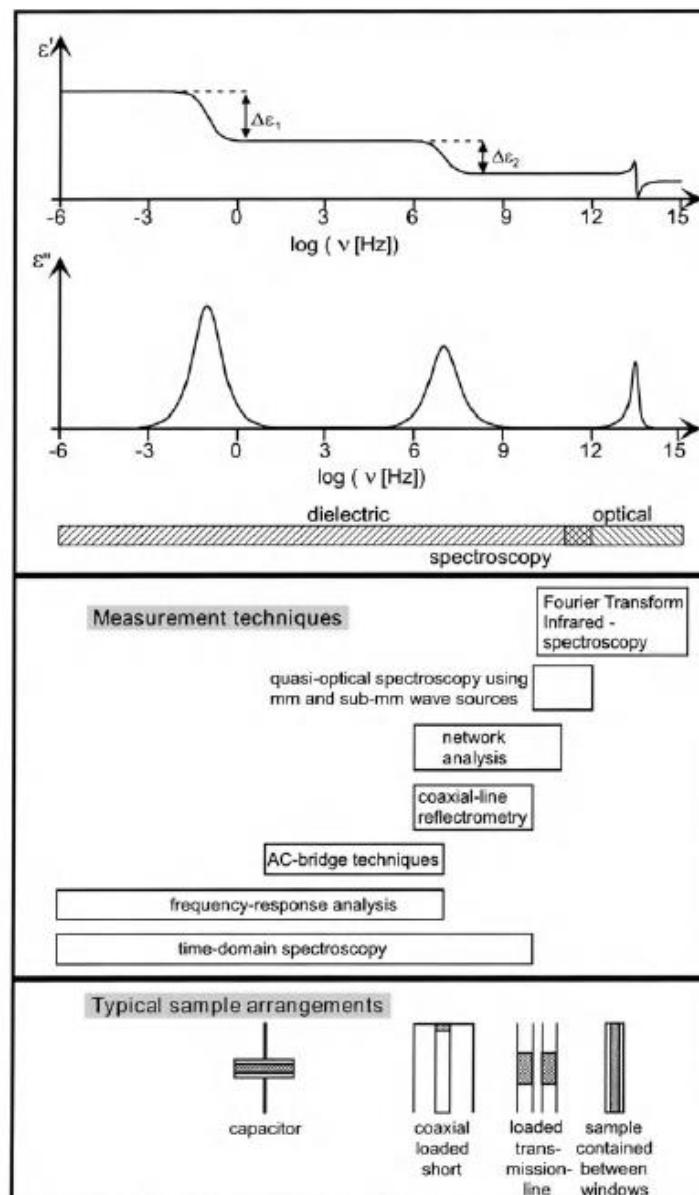


Figure 3.3 Showdown of various measurement techniques for a range of 10^{-6} to 10^{15} (Hz) "taken from [15]"

4 Mechanical properties of polymers

Mechanical properties are among the most prominent ones, mostly because they are so strongly bound with the resistance of the material and thus the reliability of products made from this material. The polymer materials can be described as viscoelastic materials. This term means, that the physical properties of the polymers change depending on the temperature, from behavior similar to solid materials to the liquid ones. This is dependent on the factor of temperature and molecular weight, which affects the speed of the deformation of molecules. This is valid for so called „slow“ deformations. The other type of deformations is encountered mostly in flowing polymer melts. The most prominently used is a stress relaxation together with the time-temperature superposition and the Boltzmann superposition principle. [3][16]

In layman's terms, the mechanical properties are so important, because their correct understanding leads to the fabrication of a durable product. When a mechanical part is used, it receives a certain amount of energy, which can lead to two scenarios. The first scenario is, that the part is broken apart, unable to handle the received amount of energy. The other scenario is, that the received energy is dissipated and the part is still functional. [16]

4.1 Tensile properties

Tensile properties are amongst the most prominent factors reflecting the durability of the material. The test of these properties is mostly conducted on so-called dumbbell shapes created from the tested material or on straight-sided specimens. These tests depend on the humidity, temperature, pretreatment of samples and deformation rate. Basically, the sample is put between two parts, from which one has a fixed position and the other is able to move on a straight line at a constant range of speed. This test can determine two important properties at one time, which are the engineering stress and engineering strain. The example of the test machine can be seen on figure below. [16]

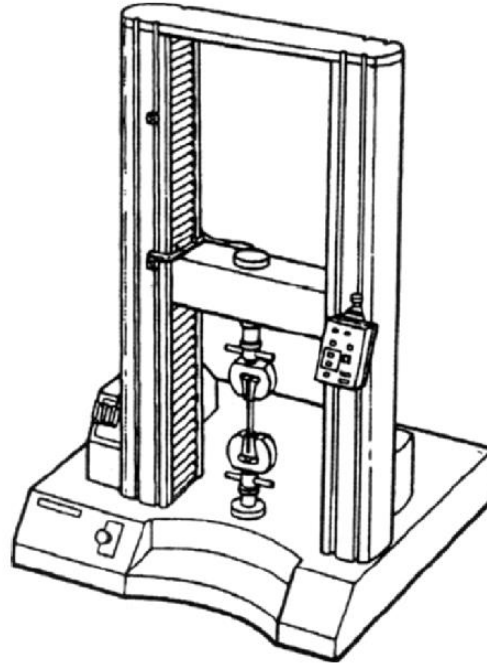


Figure 4.1 Machine for testing of mechanical properties "taken from [16]"

The engineering stress can be described with the following formula.

$$\sigma = F/A_0 \quad (4.2)$$

Where F (N) is the force applied and A_0 (mm²) is the initial cross-section area. The σ (MPa) is the tension in pull. [16]

For the engineering strain is the formula below.

$$\varepsilon = \frac{(l - l_0)}{l_0} = \frac{\Delta l}{l_0} \quad (4.3)$$

Where the l_0 (mm) represents the original length of the specimen and the l (mm) represents the current length. The elongation ε (-) (or in (%), if multiplied by 100) represents the maximal possible elongation of a material before it's break. [16]

On the figure below can be seen a typical results for these tests. The curve A represents brittle materials, curves B and C then represents durable materials and the last curve D represents the durable material without the slip limit, which is the parameter observed in this thesis. [11]

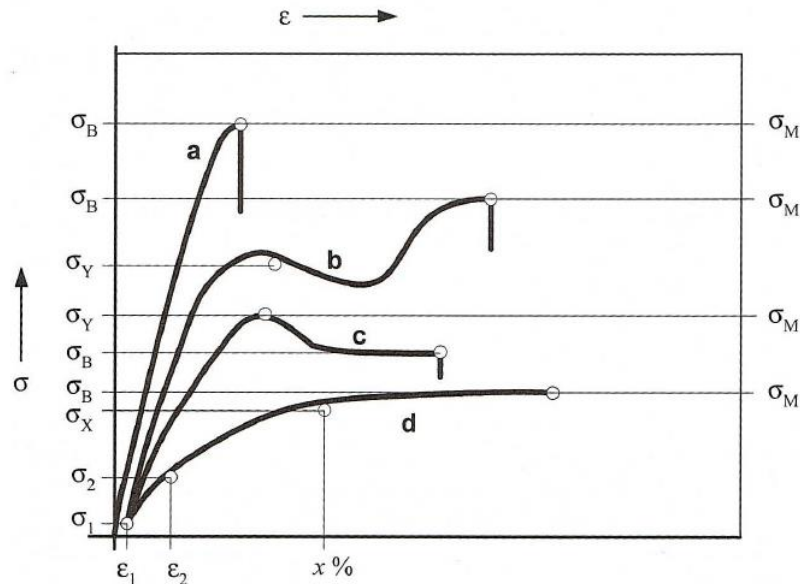


Figure 4.4 Typical results for engineering strain and stress tests "taken from [11]"

4.2 Tensile Relaxation

This characteristic specifies the ability of the material to withstand a long time deformation caused by the prolonged constant force applied in the uniaxial mode. Here, the term „internal stress“, being represented as σ_0 , is introduced, which has an origin within Kubáts' theory of relaxation from 1965. In this theory, it is assumed, that the single units of the material, such as single chains of polymers or single atoms in the case of metals, do not relax individually, but create clusters, which then relax together. Below can be seen a figure with the examples of possible results from a stress relaxation test. This characteristic is mentioned only for the purposes of introducing the mechanical properties. [16]

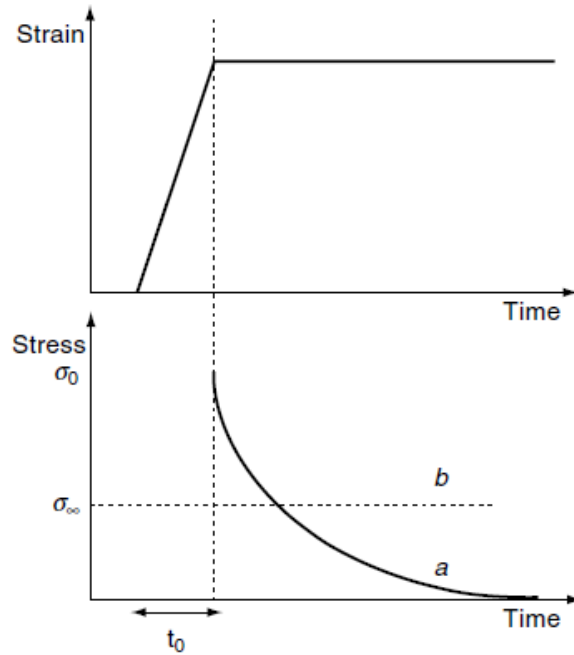


Figure 4.5 Stress relaxation test – example results "taken from [16]"

4.3 Bending and Flexure

This property represents how much can the tested material be bend before the breaking of the test sample, or reaching of the previously set angle. This is conducted by fixing the test sample and then bending it at constant speed. Main information received from this test is the flexural strength σ_{fM} (MPa) which represents the maximal pressure the material is able to withstand before it breaks. Another received information is maximal flexure s (mm) representing the distance the bent end of the sample can move from its' original position. Last is the deformation in the flexure at the maximal non-destructive tension represented by ε_{fM} (%). The flexure test is conducted with machine, which has the same precision in speed regulation as the machine used for tensile test. This characteristic was also not observed, as together with the tensile relaxation, it is mentioned for the introduction of the mechanical properties. [11]

5 PET and PEN materials

5.1 Introduction of PET and PEN thermoplastic polyesters

Both Polyethylene Terephthalate (PET) and Polyethylene Naphthalate belong to the polyester group. The PET polyester is the most commonly used thermoplastic polyester today. PET can have both semicrystalline and amorphous structure. Semicrystalline PET is characteristic with white and opaque look, while amorphous PET is transparent. The semicrystalline variant is considered to possess good strength, ductility, hardness and stiffness. The amorphous PET has less stiffness and hardness, but a better ductility to compensate. Its' water absorption is also very low [9]. The first and obvious difference between PET and PEN is in the structure of the material. Other than that, PEN is considered similar to PET regarding its' properties, with the exception of temperature resistance, which is higher to the PEN thermoplastic polyester. The structures of both polyesters are shown below. [17]

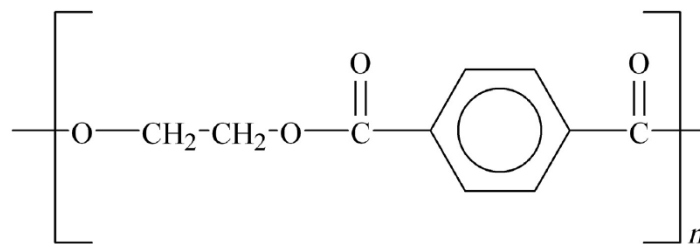


Figure 5.1 Chemical structure of PET „taken from [9]“

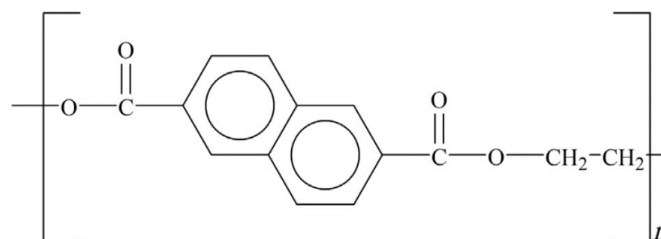


Figure 5.2 Chemical structure of PEN „taken from [17]“

On the figures above can be seen the structural difference in PET and PEN polyesters, as PEN has naphthalene rings in its' main chain. Opposed to this, PEN has benzene rings in its' main chain instead. [18]

5.2 Production of PET and PEN films

The PET polyester is produced mostly by a process, which includes two steps. In this process, Dimethyl terephthalate is being heated together with ethylene glycol. The resulting mixture of oligomers includes dihydroxyethyl terephthalate. The resulting mixture is then being heated to 250 (°C) in vacuum and this together with the presence of catalyst gives the final product. Transparent films, which are amorphous and transparent, are being created by a method called quenching, which is a rapid cooling from 190°C. Slow cooling then produces semicrystalline material. The production of fibers is realized by pushing the original heated mixture through a small hole. [2]

The PEN is being produced by a condensation polymerization of naphthalene 2,6-dicarboxylic acid with ethylene glycol. The resulting mixture can be processed in a PEN film in the exact same way as with the PET film. The main drawback for a mass production of PEN film and its' spread use was a higher price compared to PET film, as the production of 2,6-dicarboxylic acid was far more expensive. But over the time, an acceptably economical method of producing said acid was discovered and PEN film is offered for example by du Pont de Nemours and Company, or a Japanese Teijin, Ltd. [19] [20]

5.3 Comparison of PET and PEN films

The PET and PEN films are considered mostly similar in their electrical and mechanical properties. However, the PEN film is proven to be superior to the PET film. This is because “the PEN film exhibits a higher Young’s modulus, tensile strength, higher melting point and T_G , higher heat resistance, smaller thermal shrinkage coefficients, smaller water vapor/gases permeability coefficients, smaller oligomer extraction quantity, higher hydrolysis resistance, higher radiation resistance and better dielectric properties.”[19], of course, the main advantage of PET film is still it’s lower price and high availability on the market. [19]

Table 5.3 Comparison of properties of PEN and PET films „taken from [19]“

| Properties of the PEN/PET films | | |
|--|----------|----------|
| | PEN film | PET film |
| Density (g/cm ³) | 1,36 | 1,4 |
| Young's Modulus-MD (kg/mm ²) | 620 | 545 |
| Tensile Strength-MD (kg/mm ²) | 28 | 23 |
| Breaking Elongation-MD (%) | 90 | 120 |
| Melting Point (°C) | 273 | 264 |
| Tg (°C) | 113 | 69 |
| Long-term Heat Resistance (°C) | 155 | 120 |
| Thermal Shrinkage Coefficient-MD (After 30 min. at 150°C) (°C) | 0,9 | 1,5 |
| Water Vapor Permeability (g/m ² .24hr) | 6,7 | 21,3 |
| BDV (kV/mm, AC) | 340 | 325 |
| Relative Permittivity (at 25°C & 60Hz) | 3 | 3,2 |
| Dielectric Dissipation Factor (%) (at 25°C & 60Hz) | 0,3 | 0,2 |
| Volume Resistivity (Ω cm at 25°C) | 1,00E+18 | 7,00E+17 |

5.3.1 Mechanical properties

From the table above it can be seen, that the Young's modulus, which represents the tensile stiffness of a solid material, is higher for the PEN film. This is caused by the molecular chains of the PEN material, which are more rigid compared to PET. Additionally, PEN has a slower crystallization rate, which means that the PEN film can be biaxially oriented to a greater extent. [19]

5.3.2 Optical properties

The PEN film is more resistant to PET film to the sunlight exposure and the deterioration linked with it. On the other hand, regarding the transmission, PEN cannot transmit UV light below 380nm, as opposed to the UV transmission of PET, which can transmit UV light down to 310nm. Next difference found during the thermal curing of test samples shown, that the PEN changes is coloration with longer thermal exposure to yellow tones, while PET stays clearly transparent even after long-term exposure. [19] [21]

5.3.3 Radiation resistance

Regarding the radiation resistance, the PEN film is more resistant to the γ -rays exposure in vacuum, as the crosslinking occurs predominantly between PEN molecules, in opposition to scission, which occurs predominantly in PET. This is because of the structure of naphthalene ring. However, this advantage only occurs in vacuum, as the

materials are being irradiated in oxygen gas, the chance of scission of the main chains is similar in both films. [19]

5.3.4 Thermal properties

The weight loss of PEN film is shown to be better, as the weight of the PET film at 200,1°C is at 99,47% of its' original weight, compared to the PEN film with 99,64% at the exact same temperature which was shown by the preliminary test. The preliminary test also showed, that the heat flow for PET and PEN films can be considered similar with - 0,3605 W/g till 200 °C (Fig. 6.1.). The melting point for PEN is slightly higher compared to PET in both the expected values and values gained through the preliminary test. [19]

5.3.5 Electrical properties

Due to the difference in composition of PET and PET polyesters the dielectric properties differ by a great margin. This is caused by the naphthalate rings in the monomer chains of PEN film contribute to the higher rigidity of the whole chain, which means, that the polarization of PEN film is lower compared to the phenyl group. This is the cause for higher permittivity of PET film compared to PEN in many measurements. [22]

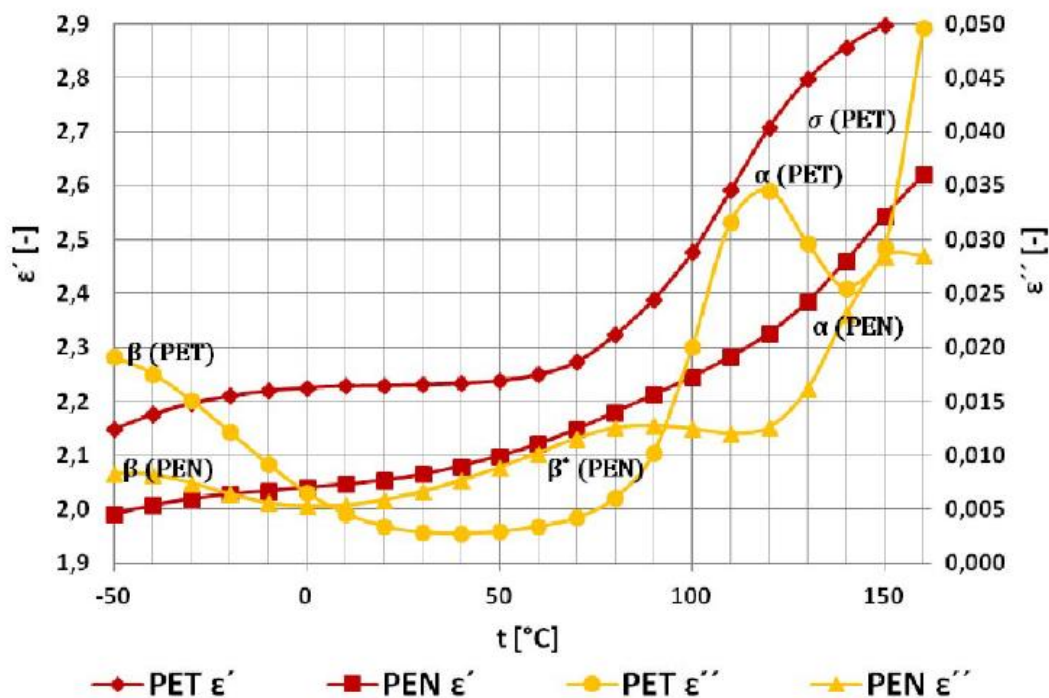


Figure 5.4 “Dependance of the real and imaginary parts of complex permittivity of PET and PEN films on temperature at 50Hz frequency” “taken from [22]”

5.4 Usage of PET and PEN materials

5.4.1 Usage of PET material

Polyethylene is one of the most widely produced type of plastic in the world [23]. Because of its' availability and cheap cost, PET material is used in a wide variety of applications. Because it absorbs very little to nearly no water, it is often used in food industry for the manufacture of water bottles, food trays and roasting bags [17]. Next usages are as video/audio tapes, various mechanical components and floppy discs (last one is of historical usage mostly) [19]. Another interesting usage is in electric industry. For example, on a thin PET film can be printed a dipole antenna, which with its' flexibility has uses in specific applications such as remote controller or set top box [24]. Also semiconductor components can be printed on a PET film base as for example high-performance ZnO thin-film transistor which structure is also shown below. [17][19][23][24][25]

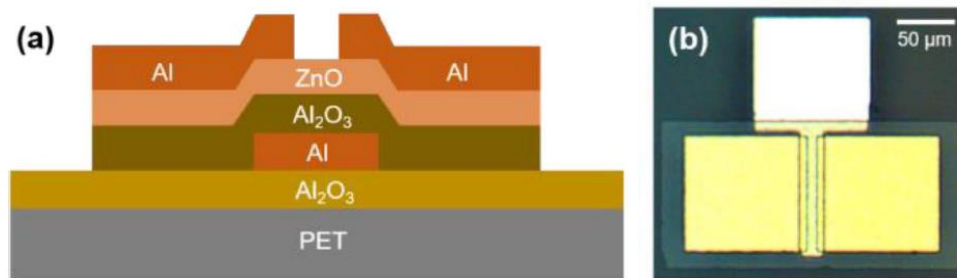


Figure 5.5 Schematic of a structure of ZnO TFTs(a) and top-view micrograph(b) “taken from [25]“

5.4.2 Usage of PEN material

The PEN material is, because of its' higher cost, mostly used in electrical or other technically-oriented industries. It is also used in the manufacture of general-purpose, high-value-added applications in labels, laminates and various circuitry [17]. It showed its' superiority in usage over the PET material mainly in for example hermetic motor manufacture or videotape production [19]. Because of its' excellent hydrolytic resistance, it is especially valued in hermetic motor uses as for small home refrigerators. Also, its' high heat-resistance in the form of an extremely thin film, miniaturized, heat-resistant capacitors can be manufactured with its' use [19]. Another supposed use is for example in electrostatically controlled transparent MEMS display. The protecting layer is usually made by glass, which is speculated to be replaced by a PEN film and thus produce a flexible variant of such display [26]. Other uses can be for example as a membrane in a microphone device. [17][19][26]

6 Samples preparation and test procedures

6.1 Basic description of test samples

The samples were made from PET (MYLAR® A, Teijin DuPont) and PEN (TEONEX® Q51, Teijin DuPont) thin films. The Average thickness is 0,029 mm for PEN and 0,034 mm for PET (average from 50 measurements, variation coefficient lower than 6%). The shape of the test samples for dielectric properties is a square with dimensions of 3,5×3,5 cm. For the samples dedicated for mechanical tension test, the exact shape and dimensions are described in more detail in the next chapter. Samples for dielectric test were cut by hand with the usage of scissors while the mechanical tension test samples were made on the press. For each time of extraction were made 5 testing samples from each material, with total of 90 samples for tests regarding dielectric properties and 90 samples for mechanical tests. All of the samples were conditioned in a room temperature of 25 °C and air humidity of 45 %.

The next stage was the conditioning of the samples by a long-term exposure to a high temperature. It was decided, that the temperature, in which the samples will be conditioned, will be set to 190 (°C) and the times of sampling is 0(h), 150(h), 300(h), 500(h), 1000(h), 1500(h), 2000(h), 3000(h) and 4000(h).

The preliminary tests showed that there are no changes to the materials at 200 °C and the melting points of both PET and PEN materials were also discovered. Thus, it was decided the temperature of exposure.

Table 6.1 Melting temperatures of PET and PEN films [19]

| Melting points | measured (°C) | expected (°C) |
|----------------|---------------|---------------|
| PET | 253 | 264 |
| PEN | 266 | 273 |

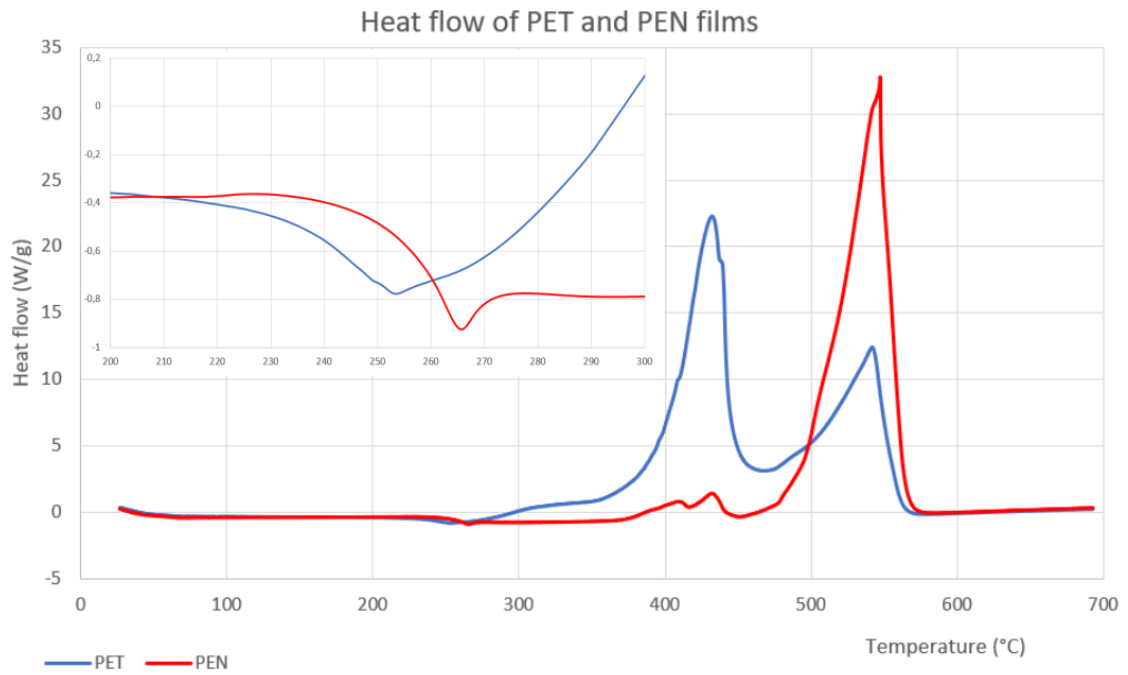


Figure 6.2 Heat flow of PET and PEN films (detail from 200 to 300 °C)



Picture 6.3 Thermal conditioning of PET and PEN films in an oven

6.2 Tensile properties

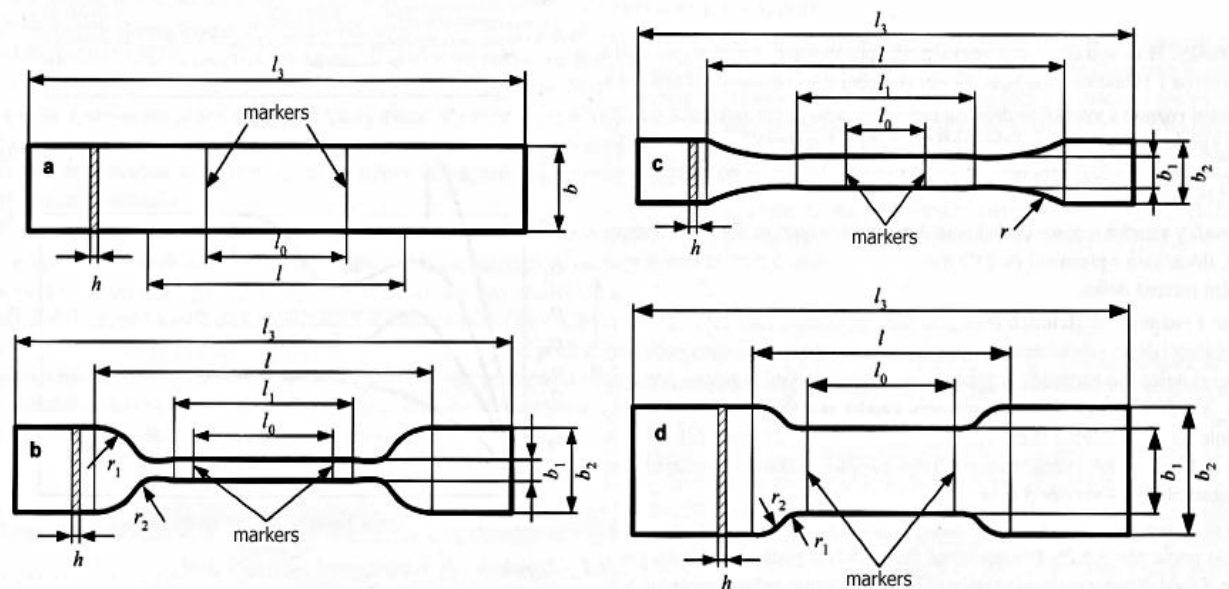
The dimensions and process of testing the tensile properties of plastic materials is described by the norm ČSN ISO 521. This norm specifies the dimensions of the samples, minimal number of test runs of 5 and the testing conditions. [6]

6.2.1 Shape and dimensions

The shape and dimensions for thin desks and foil materials is as follows:

Table 6.4 Dimensions of the test samples for thin desks and foil materials "taken from [11]"

| Dimension / test specimen | | a | b | c | d |
|---------------------------|----------------------------|--------------|---------------|--------------|----------------|
| b | width | 10 to 25 | | | |
| b_1 | width of narrowed end part | | $6 \pm 0,4$ | $10 \pm 0,2$ | $25,4 \pm 0,1$ |
| b_2 | end width | | 25 ± 1 | $20 \pm 0,5$ | 38 |
| h | thickness | ≤ 1 | ≤ 1 | ≤ 1 | ≤ 1 |
| l_0 | initial measured length | $50 \pm 0,5$ | $25 \pm 0,25$ | $50 \pm 0,5$ | $50 \pm 0,5$ |
| l | initial jaws distance | 100 ± 5 | 80 ± 5 | 115 ± 5 | 73,4 |
| l_3 | full length | ≥ 150 | ≥ 115 | ≥ 150 | 152 |
| r | radius | | | ≥ 60 | |
| r_3 | small radius | | 25 ± 2 | | 22 |
| r_2 | large radius | | 25 ± 2 | | 25,4 |



Scheme 6.5 Dimensions for testing samples as set by the norm ČSN ISO 521 "taken from [11]"

Shape **a** is the basic shape of the test sample, **b** is recommended for materials with high elongation at break, **c** is for rigid boards and **d** for flexible boards. The samples are made by machining of the material or by stamping with a sharp form on a press. At no point during the process should occur any imperfections of the testing sample edge. For this experiment is used a shape **b**. [11]



Picture 6.6 Press used in fabrication of test samples

6.2.2 Testing procedure

The samples are to be conditioned for 24 hours in standard conditions, which are 23 ± 2 °C and 50 ± 5 % of air humidity. Furthermore, it is important to take a special care when the samples are being put into the jaws. The sample cannot slip out of the jaws at no point during the testing, nor should the sample be damaged by the jaws pressure. The sample should take the right angle with the jaws and be in correlation with the direction of the movement. The sample should not be in tension before the start of the procedure. [11]



Picture 6.7 Mechanical test of PEN foil

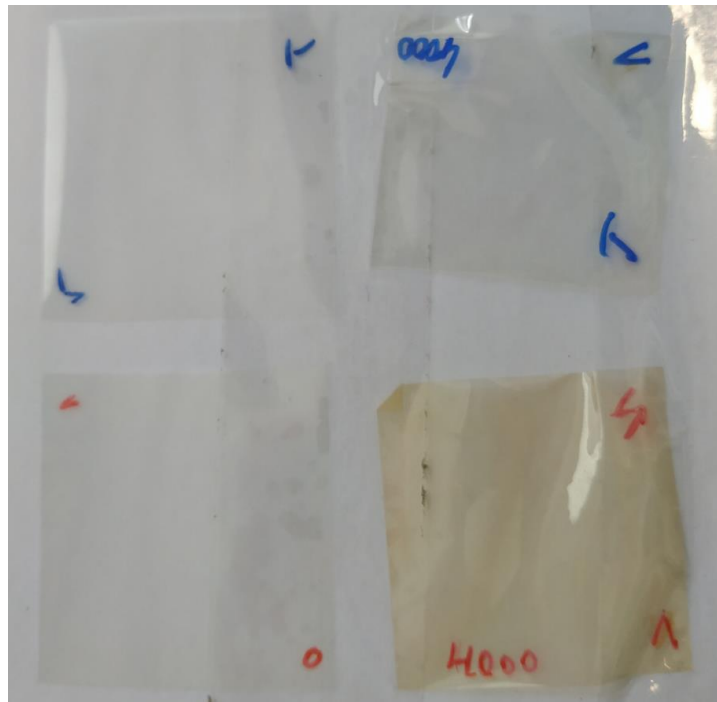
The mechanical tests proved to be especially challenging, mainly because of the embrittlement of both PET and PEN foils during the long-term thermal exposure, as the samples tend to fall apart during any manipulation. The PEN foil proved to be less prone to this, as the embrittlement became apparent after the exposure of more than 1000(h). The PET foil became very brittle after even the shortest of exposure.

6.3 Dielectric properties

For the dielectric properties, it is needed to measure the complex permittivity and through these results, to calculate the loss factor $\text{tg}\delta$. The good insulation material is considered with $\text{tg}\delta < 10^{-3}$ and a bad one with $\text{tg}\delta > 10^{-2}$. For the optimal evaluation of the material, it is good to know the following characteristics [11]:

- Frequency characteristic: $\text{tg}\delta = f(U)$ – dependance on frequency during set AC voltage and set temperature
- Voltage characteristic: $\text{tg}\delta = f(f)$ – dependance on AC voltage during set frequency and temperature
- Temperature characteristic: $\text{tg}\delta = f(v)$ – dependance on temperature during set frequency and AC voltage

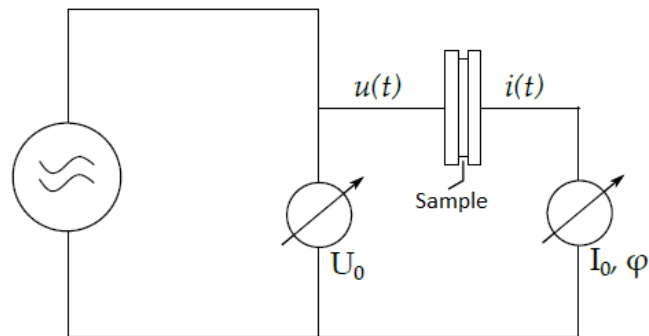
For the measurement of the relative permittivity ϵ_r was chosen broadband dielectric spectroscopy. Only the Frequency characteristics were measured because of the time and material limitation (nitrogen consumption during testing), with constant voltage of 1 (V) and a constant room temperature of 25 (°C). The air humidity was a constant at 45(%).



Picture 6.8 Test samples of PET (top) and PEN (bottom), before thermal aging (left) and after thermal aging at 190 °C for 4000h (right)

6.3.1 Testing procedure

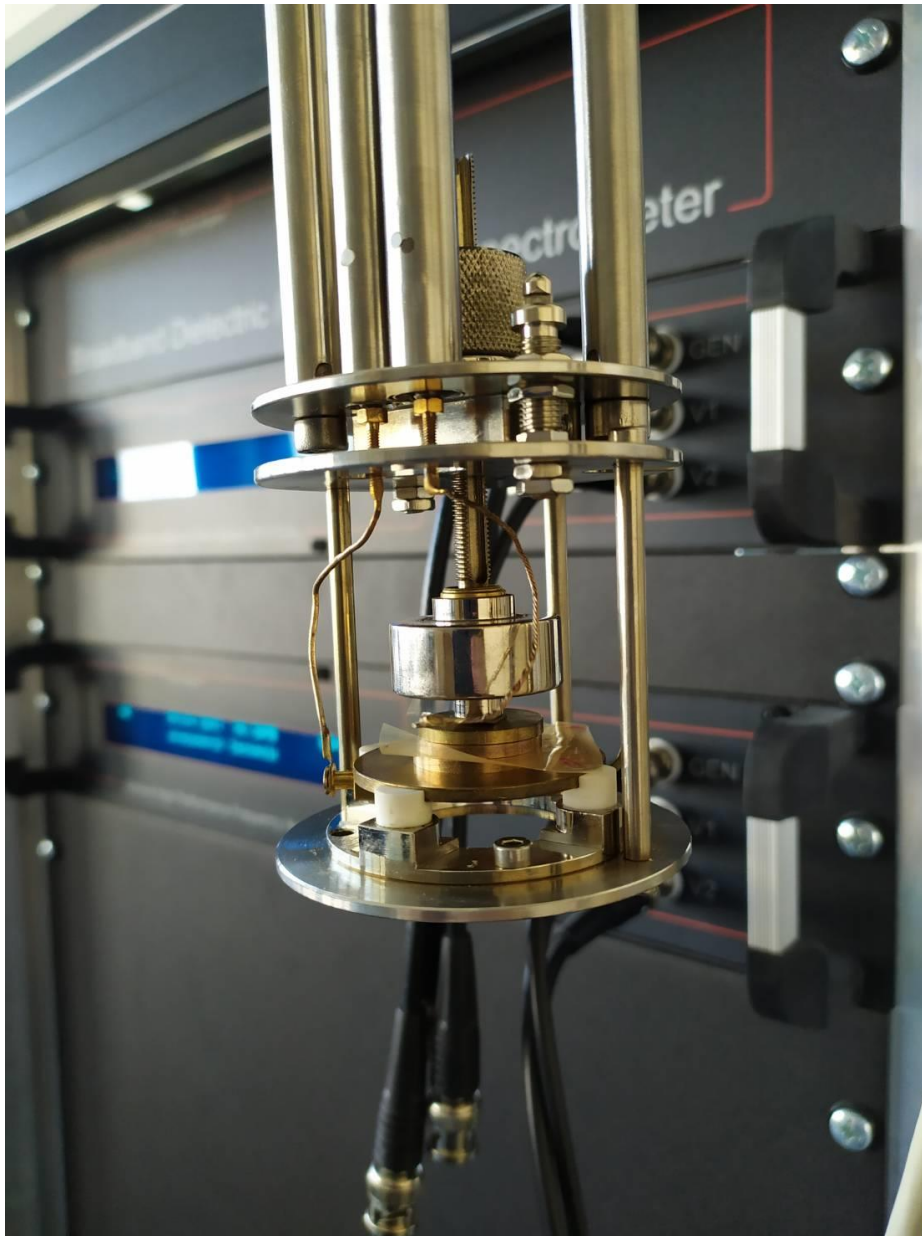
For the Broadband dielectric spectroscopy (BDS) was used a device Novocontrol Alpha A. This device measures voltage $u(t)$ and current $i(t)$ during the application of AC voltage of specific frequency. This allows the calculation of amplitude of a current I_0 and the phase angle of the base harmonic $i^*(t)$ by the Fourier transformation of the signal $i(t)$. The basic principle of the device is shown in the block diagram. For this measurement were used electrodes with diameter of $\varnothing 20$ (mm). [14]



Scheme 6.9 Block diagram of Novocontrol Alpha A “taken from [14]“



Picture 6.10 Novocontrol Alpha A



Picture 6.11 Sample od PEN foil prepared for BDS in Novocontrol Alpha A

The measurement of dielectric properties by BDS proved much less challenging. It was nonetheless needed to take special care during the manipulation with the samples because of the high brittleness after the long-term thermal exposure. Another important thing to take care of was, that the electrodes around the sample had to be in an alignment with each other as much as possible. The room temperature and air humidity of the room were checked frequently to ensure the proper conditions for testing.

7 Results

7.1 Mechanical test results

The first test results presented were obtained during the tensile test, and show the mechanical properties of the materials, namely the engineering stress σ (MPa) and percentual elongation of the materials ε (%).

Table 7.1 Results of the mechanical tests (detailed results in attachment A and B)

PET

| T (h) | σ aver. (MPa) | ε aver. (%) |
|-------|----------------------|-------------------------|
| 0 | 146,000 | 43,880 |
| 150 | 89,233 | 1,562 |
| 300 | 16,556 | 0,115 |
| 500 | 30,654 | 0,272 |
| 1000 | 20,833 | 0,290 |
| 1500 | 24,167 | 0,413 |
| 2000 | 17,250 | 0,228 |
| 3000 | 13,300 | 0,465 |
| 4000 | 11,633 | 0,558 |

PEN

| T (h) | σ aver. (MPa) | ε aver. (%) |
|-------|----------------------|-------------------------|
| 0 | 137,133 | 24,246 |
| 150 | 127,267 | 10,514 |
| 300 | 132,583 | 10,522 |
| 500 | 136,167 | 9,356 |
| 1000 | 125,950 | 6,740 |
| 1500 | 66,133 | 1,140 |
| 2000 | 76,771 | 4,693 |
| 3000 | 61,063 | 1,318 |
| 4000 | 94,050 | 3,842 |

As can be seen from the results above, the PEN film came from the test as an overall superior material, even though the average elongation ε (%) and tension in pull σ (MPa) is slightly higher in PET for 0 h of thermal exposure. To the contrary, the PEN film keeps its' mechanical properties after far longer exposure to the high temperature than PET film. Although, it has to be stated, that albeit rarely, some individual values came to be relatively high even for PET. Theoretically, the materials are able to maintain their tension in pull endurance σ (MPa) at high values, but unfortunately, this is in practical terms impossible. The PET material starts to be extremely brittle even after the shortest duration of the exposure, which greatly complicates any manipulation with the samples, as the samples tend to fall apart through the combination of brittleness and the warping of the film. The PEN film keeps its' flexibility longer, but is also not immune to this effect. This setback could be countered by testing a film with greater thickness, as the PET and PEN films tested seem to be too thin to give more accurate results with the fabrication and testing method available.

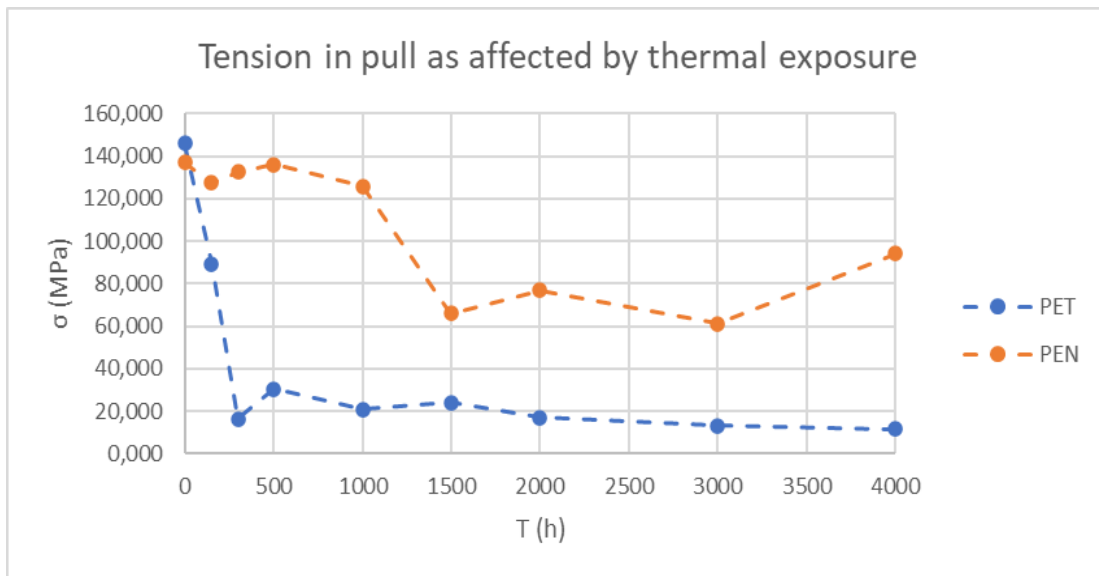


Figure 7.2 Tension in pull as affected by thermal exposure – comparison of PET and PEN films

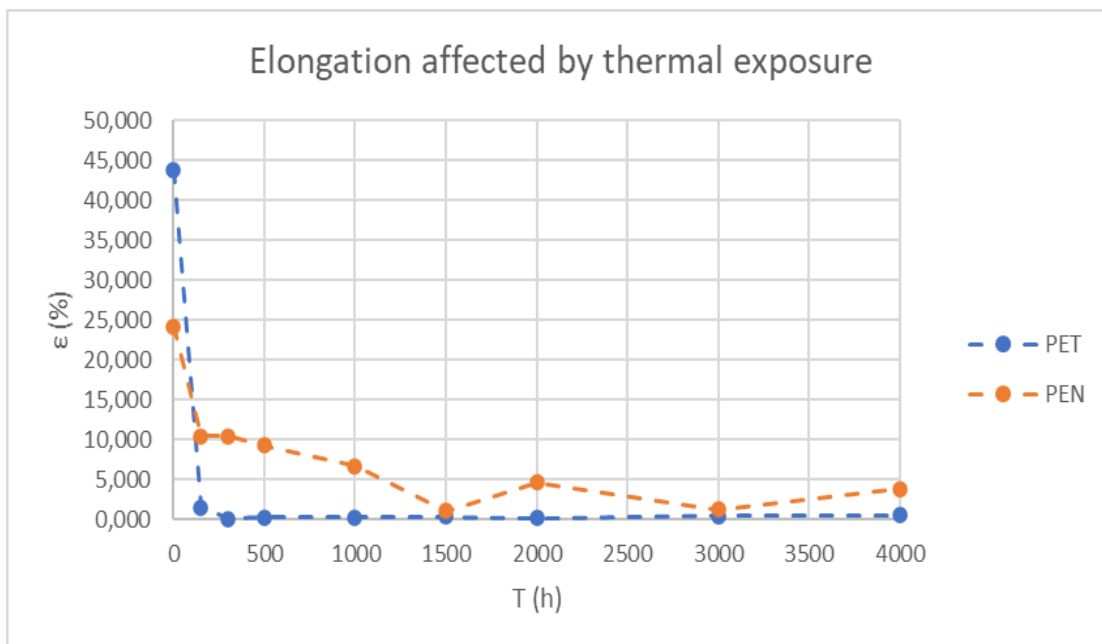


Figure 7.3 Percentual elongation as affected by thermal exposure – comparison of PET and PEN films

7.2 Electrical properties in frequency range – results

The second test results presented show the electrical properties of the PET and PEN thin films in a frequency range. The exact property observed is the dielectric loss factor $\text{tg } \delta$ (-), as it seems to be the best indicator of the changes caused by the thermal exposure. The results are presented mainly via figures, as the tables are very large. For this reason, 6 frequencies were chosen across the range the tables with the results can be found in an attachment C and D.

It can be seen from the figures below, that there is a difference in the materials regarding the reaction of the dielectric loss factor to the increasing frequency. The trend of the loss factor in PET film seem to be an increase together with the rising frequency of the electric field, while the PEN film seem to keep a relative stability at a set value. This shows, that PEN film is a good insulation material as its' dielectric loss factor value for 0 h of thermal exposure is set under 10^{-3} in the entire measured frequency range. The PET film also has the properties for being classified as a good insulation material, especially at the low frequencies, most important of them being the 50 (Hz). But unfortunately, because of the rising dielectric loss factor together with a rising frequency, it has to be evaluated as the inferior one compared to PET. Its' loss factor $\text{tg } \delta$ (-) does not reach the line of 10^{-2} to be classified as a bad insulation material, but it slightly rises over the value of 10^{-3} .

Regarding the thermal exposure, its' effect is mostly observable during low frequency range. During high frequencies, the electric polarizability is the most prominent, while on the low frequencies, other types of polarizability (such as dipole and atomic polarizability) also contribute to the total. The electric polarizability seem to not being affected in great margin by any long-term thermal exposure. On the low frequencies can be seen the difference in reactions of each material to the thermal exposure, as the PET film keeps its' original value of dielectric loss factor and does not seem to change by any meaningful margin, while the PEN films' dielectric loss factor rises steadily. Interestingly, for the PET film, it seem like, the transition between 3000 h and 4000 h of thermal exposure seem to start affecting the internal structure of the polymer, as its' dielectric loss factor increases by a great margin.

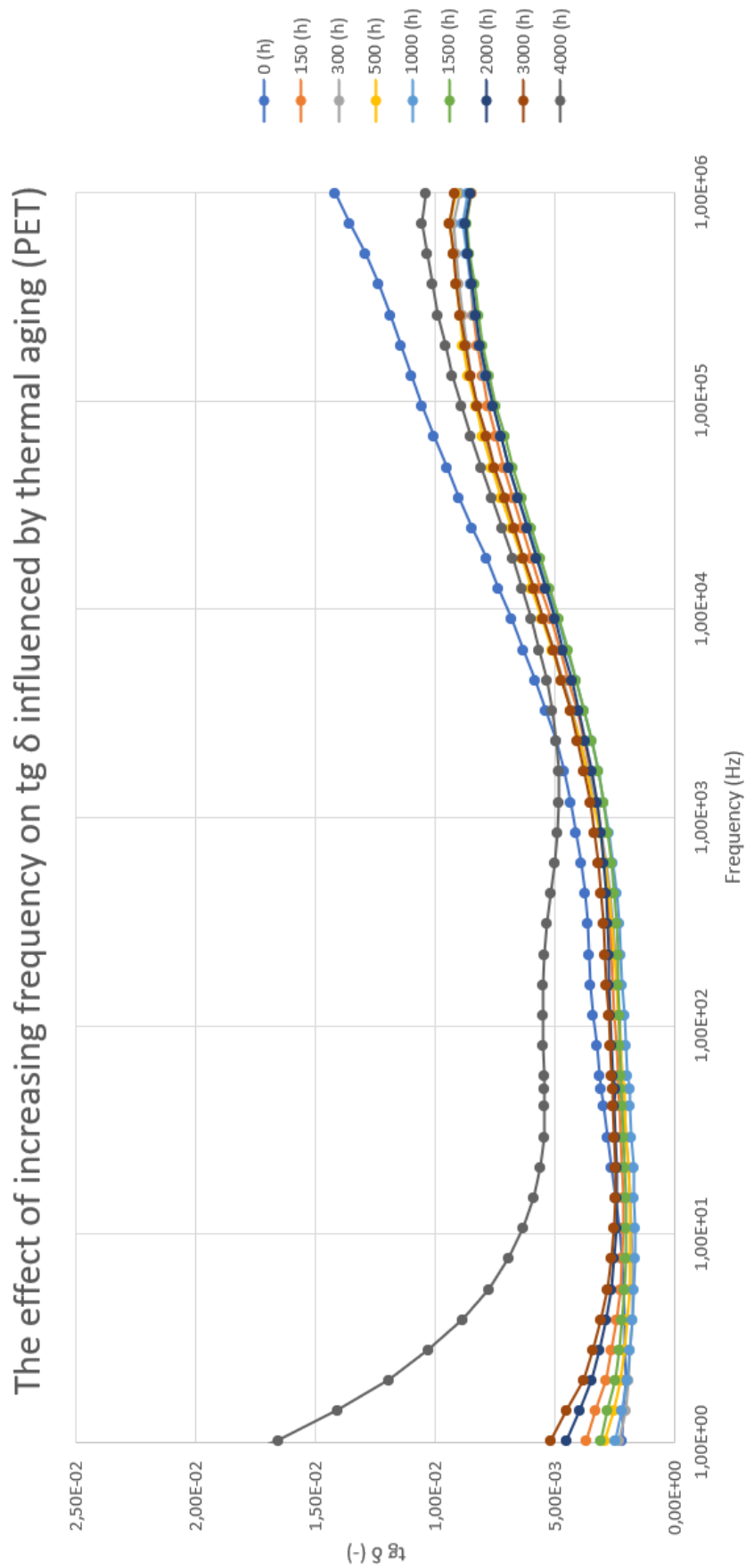


Figure 7.4 The effect of thermal exposure on the dielectric loss factor $\text{tg } \delta$ in measured frequency range (PET)

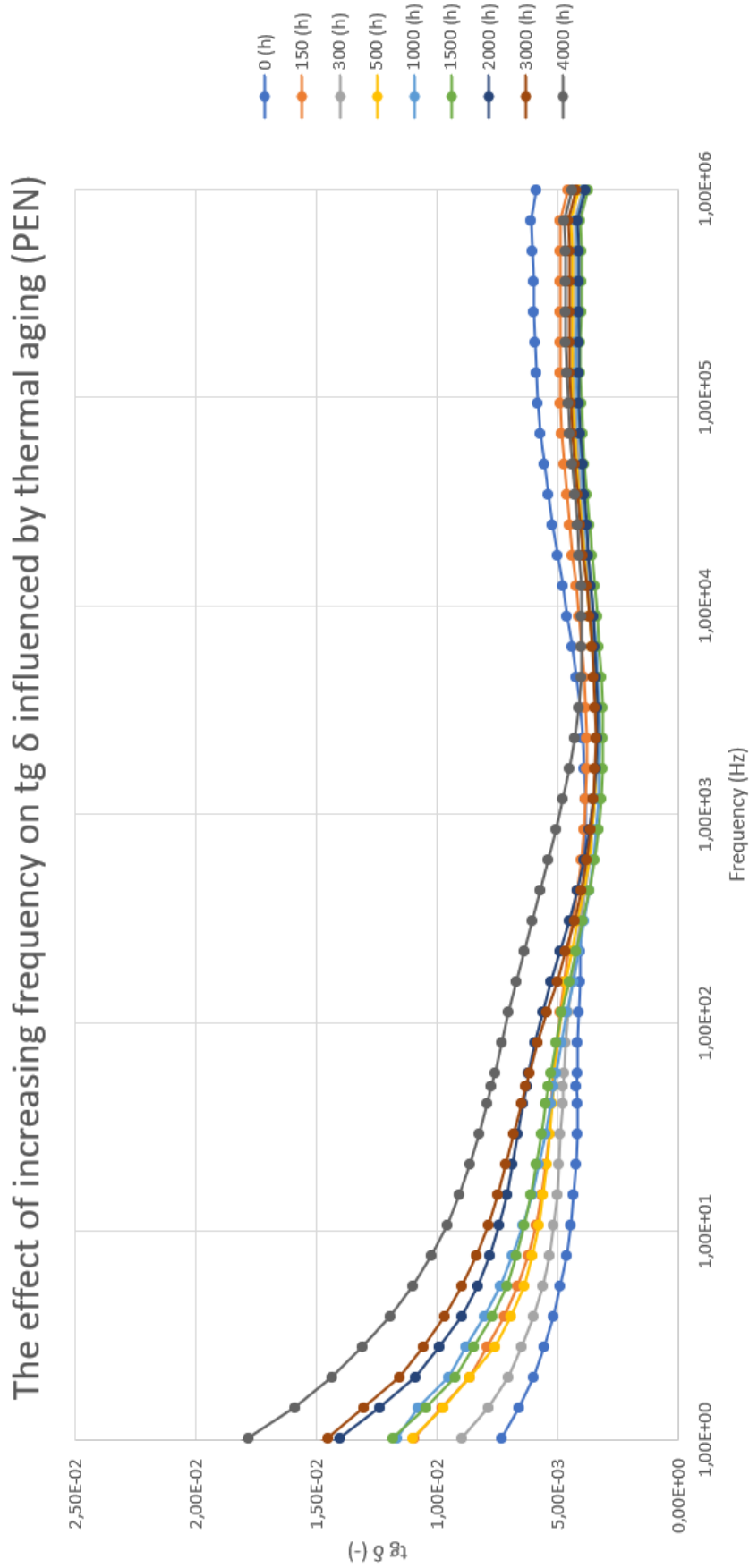


Figure 7.5 The effect of thermal exposure on the dielectric loss factor $tg \delta$ in measured frequency range (PEN)

Conclusion

The main objective of this thesis was to introduce the properties of PET and PEN thin films, their comparison and to observe the effect of long-term thermal exposure on the mechanical and dielectric properties of these materials via tests of prepared and thermally aged samples. In the comparison of basic properties, it can be seen, that the PEN film should be a superior material regarding the physical properties examined in this thesis. Overall, this has proven to be true, as both preliminary test and the main tests showed mechanical and dielectric properties to be better compared to the PET film. PEN film, compared to PET film, has a slightly higher melting point, keeps an overall lower dielectric loss factor though the entire measured frequency range and is on par with PET film in tension in pull endurance. The only exception is the percentual elongation of non-aged materials, in which the PET seem to have higher elongation compared to PEN by roughly 45 % .

Regarding the effect of thermal aging on the mechanical properties, PEN film is clearly superior, as it sustains good mechanical properties even after 1000 h of the exposure. The PET film, on the other hand, tend to become very brittle and twists even after the shortest time of samplings. This happens even to PET film after sufficiently low exposure. The dielectric properties seem to be affected by the thermal exposure mostly in low frequency range. This may be, because in high frequencies, the loss factor is mostly being contributed by electric type of polarization, which seem to be not affected by thermal aging. During low frequencies, other types of polarization (such as dipole or atomic) also contribute to the total. Those types of polarization are being affected by the thermal exposure, as it can be expected, that the thermal aging affects the inner structure of the material. Interestingly, PET seem to be more resistant to the thermal aging effect overall for relatively short periods of time, as it kept its' dielectric loss factor relatively stable. It is not fully resistant to this effect however, as it seem, that during the transition between 3000 h and 4000 h the thermal exposure starts to affect its' inner structure , thus its' loss factor increase by a great margin. The PEN films' dielectric loss factor rises steadily through the whole process of thermal aging. It has to be noted, that despite this, both materials can be classified as good insulation material as their loss factor never cross the value of 10^{-2} .

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Attachments

Attachment A – Mechanical test results (PET)

PET

| T (h) | Fmax (N) | ϵ (%) | σ [MPa] | σ aver. (MPa) | St. deviation | ϵ aver. (%) | St. deviation |
|-------|----------|----------------|----------------|----------------------|---------------|----------------------|---------------|
| 0 | 18,500 | 53,580 | 154,167 | 146,000 | 17,746 | 43,880 | 7,738 |
| | 18,240 | 38,540 | 152,000 | | | | |
| | 18,660 | 33,940 | 155,500 | | | | |
| | 13,720 | 45,540 | 114,333 | | | | |
| | 18,480 | 47,800 | 154,000 | | | | |
| 150 | 15,100 | 1,625 | 125,833 | 89,233 | 49,558 | 1,562 | 1,359 |
| | 2,000 | 0,150 | 16,667 | | | | |
| | 7,000 | 0,250 | 58,333 | | | | |
| | 14,270 | 2,640 | 118,917 | | | | |
| | 15,170 | 3,146 | 126,417 | | | | |
| 300 | 2,300 | 0,160 | 19,167 | 16,556 | 7,436 | 0,115 | 0,040 |
| | 0,980 | 0,100 | 8,167 | | | | |
| | 2,680 | 0,084 | 22,333 | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| 500 | 1,665 | 0,080 | 13,875 | 30,654 | 23,729 | 0,272 | 0,272 |
| | 5,692 | 0,464 | 47,433 | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| 1000 | 0,800 | 0,200 | 6,667 | 20,833 | 20,035 | 0,290 | 0,127 |
| | 4,200 | 0,380 | 35,000 | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| 1500 | 4,500 | 0,360 | 37,500 | 24,167 | 14,743 | 0,413 | 0,284 |
| | 3,200 | 0,160 | 26,667 | | | | |
| | 1,000 | 0,720 | 8,333 | | | | |
| | N/A | N/A | N/A | | | | |
| | N/A | N/A | N/A | | | | |
| 2000 | 0,500 | 0,200 | 4,167 | 17,250 | 11,202 | 0,228 | 0,097 |
| | 1,700 | 0,380 | 14,167 | | | | |
| | 1,300 | 0,260 | 10,833 | | | | |
| | 3,850 | 0,160 | 32,083 | | | | |
| | 3,000 | 0,140 | 25,000 | | | | |
| 3000 | 0,900 | 0,260 | 7,500 | 13,300 | 7,232 | 0,465 | 0,346 |
| | 2,780 | 0,064 | 23,167 | | | | |
| | 1,900 | 0,900 | 15,833 | | | | |
| | 1,800 | 0,740 | 15,000 | | | | |
| | 0,600 | 0,360 | 5,000 | | | | |
| 4000 | 3,000 | 1,400 | 25,000 | 11,633 | 9,514 | 0,558 | 0,489 |
| | 2,200 | 0,500 | 18,333 | | | | |
| | 0,430 | 0,200 | 3,583 | | | | |
| | 0,780 | 0,230 | 6,500 | | | | |
| | 0,570 | 0,460 | 4,750 | | | | |

Attachment B – Mechanical test results (PEN)**PEN**

| T (h) | Fmax (N) | ϵ (%) | σ (MPa) | σ aver. (MPa) | St. deviation | ϵ aver. (%) | St. deviation |
|-------|----------|----------------|----------------|----------------------|---------------|----------------------|---------------|
| 0 | 16,900 | 23,780 | 140,833 | 137,133 | 10,054 | 24,246 | 2,420 |
| | 15,230 | 23,710 | 126,917 | | | | |
| | 15,580 | 25,670 | 129,833 | | | | |
| | 16,290 | 20,810 | 135,750 | | | | |
| | 18,280 | 27,260 | 152,333 | | | | |
| 150 | 16,550 | 11,190 | 137,917 | 127,267 | 8,454 | 10,514 | 0,562 |
| | 14,780 | 9,960 | 123,167 | | | | |
| | 15,820 | 10,110 | 131,833 | | | | |
| | 13,880 | 11,040 | 115,667 | | | | |
| | 15,330 | 10,270 | 127,750 | | | | |
| 300 | 16,780 | 10,620 | 139,833 | 132,583 | 6,204 | 10,522 | 0,807 |
| | 15,450 | 11,380 | 128,750 | | | | |
| | 15,840 | 11,110 | 132,000 | | | | |
| | 14,970 | 9,350 | 124,750 | | | | |
| | 16,510 | 10,150 | 137,583 | | | | |
| 500 | 15,780 | 8,830 | 131,500 | 136,167 | 7,747 | 9,356 | 0,537 |
| | 17,100 | 9,950 | 142,500 | | | | |
| | 16,880 | 9,360 | 140,667 | | | | |
| | 14,970 | 8,810 | 124,750 | | | | |
| | 16,970 | 9,830 | 141,417 | | | | |
| 1000 | 17,610 | 10,160 | 146,750 | 125,950 | 22,918 | 6,740 | 3,016 |
| | 13,940 | 4,140 | 116,167 | | | | |
| | 14,910 | 5,010 | 124,250 | | | | |
| | 17,870 | 9,890 | 148,917 | | | | |
| | 11,240 | 4,500 | 93,667 | | | | |
| 1500 | 11,980 | 3,140 | 99,833 | 66,133 | 21,957 | 1,140 | 1,135 |
| | 4,900 | 0,400 | 40,833 | | | | |
| | 7,200 | 0,600 | 60,000 | | | | |
| | 6,900 | 0,620 | 57,500 | | | | |
| | 8,700 | 0,940 | 72,500 | | | | |
| 2000 | 23,650 | 17,470 | 197,083 | 76,771 | 80,677 | 4,693 | 8,520 |
| | 4,700 | 0,500 | 39,167 | | | | |
| | 3,000 | 0,200 | 25,000 | | | | |
| | 5,500 | 0,600 | 45,833 | | | | |
| | N/A | N/A | N/A | | | | |
| 3000 | 15,810 | 4,390 | 131,750 | 61,063 | 47,492 | 1,318 | 2,051 |
| | 3,500 | 0,160 | 29,167 | | | | |
| | 5,000 | 0,360 | 41,667 | | | | |
| | 5,000 | 0,360 | 41,667 | | | | |
| | N/A | N/A | N/A | | | | |
| 4000 | 17,120 | 6,180 | 142,667 | 94,050 | 45,892 | 3,842 | 2,739 |
| | 6,000 | 0,800 | 50,000 | | | | |
| | 12,860 | 4,790 | 107,167 | | | | |
| | 15,450 | 6,400 | 128,750 | | | | |
| | 5,000 | 1,040 | 41,667 | | | | |

Attachment C – Dielectric properties in frequency range test results (PET)

| PET | 0 (h) | | 150 (h) | | 300 (h) | |
|------------|----------------|---------------|--------------|---------------|--------------|---------------|
| | Frequency (Hz) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) |
| 5,00E-01 | 2,60E-03 | 6,08E-04 | 5,41E-03 | 3,46E-03 | 3,05E-03 | 8,84E-04 |
| 5,21E-01 | 2,61E-03 | 5,25E-04 | 5,21E-03 | 3,55E-03 | 3,03E-03 | 8,74E-04 |
| 7,29E-01 | 2,42E-03 | 4,79E-04 | 4,48E-03 | 2,82E-03 | 2,64E-03 | 6,82E-04 |
| 1,02E+00 | 2,22E-03 | 3,93E-04 | 3,72E-03 | 2,19E-03 | 2,31E-03 | 5,63E-04 |
| 1,43E+00 | 2,17E-03 | 1,89E-04 | 3,31E-03 | 1,83E-03 | 2,09E-03 | 4,20E-04 |
| 2,00E+00 | 2,08E-03 | 2,28E-04 | 2,87E-03 | 1,45E-03 | 1,95E-03 | 3,24E-04 |
| 2,80E+00 | 2,12E-03 | 1,97E-04 | 2,64E-03 | 1,23E-03 | 1,88E-03 | 2,52E-04 |
| 3,92E+00 | 2,10E-03 | 1,70E-04 | 2,42E-03 | 1,05E-03 | 1,78E-03 | 2,02E-04 |
| 5,49E+00 | 2,15E-03 | 1,82E-04 | 2,29E-03 | 8,77E-04 | 1,77E-03 | 1,39E-04 |
| 7,68E+00 | 2,23E-03 | 1,78E-04 | 2,21E-03 | 7,41E-04 | 1,78E-03 | 1,03E-04 |
| 1,08E+01 | 2,35E-03 | 2,11E-04 | 2,19E-03 | 6,59E-04 | 1,82E-03 | 9,12E-05 |
| 1,51E+01 | 2,48E-03 | 2,36E-04 | 2,19E-03 | 6,02E-04 | 1,89E-03 | 8,63E-05 |
| 2,11E+01 | 2,64E-03 | 2,69E-04 | 2,22E-03 | 5,51E-04 | 1,96E-03 | 8,56E-05 |
| 2,95E+01 | 2,81E-03 | 3,03E-04 | 2,28E-03 | 5,24E-04 | 2,04E-03 | 8,67E-05 |
| 4,13E+01 | 2,99E-03 | 3,48E-04 | 2,35E-03 | 5,08E-04 | 2,13E-03 | 8,42E-05 |
| 5,00E+01 | 3,12E-03 | 3,38E-04 | 2,38E-03 | 4,72E-04 | 2,20E-03 | 1,03E-04 |
| 5,78E+01 | 3,14E-03 | 3,46E-04 | 2,41E-03 | 4,99E-04 | 2,21E-03 | 8,07E-05 |
| 8,10E+01 | 3,29E-03 | 3,53E-04 | 2,47E-03 | 5,06E-04 | 2,28E-03 | 9,15E-05 |
| 1,13E+02 | 3,44E-03 | 3,30E-04 | 2,54E-03 | 4,93E-04 | 2,36E-03 | 7,29E-05 |
| 1,59E+02 | 3,54E-03 | 3,31E-04 | 2,59E-03 | 5,08E-04 | 2,43E-03 | 7,75E-05 |
| 2,22E+02 | 3,59E-03 | 3,14E-04 | 2,64E-03 | 5,05E-04 | 2,50E-03 | 7,67E-05 |
| 3,11E+02 | 3,67E-03 | 3,04E-04 | 2,72E-03 | 4,97E-04 | 2,60E-03 | 8,09E-05 |
| 4,36E+02 | 3,78E-03 | 2,87E-04 | 2,81E-03 | 4,88E-04 | 2,73E-03 | 8,51E-05 |
| 6,10E+02 | 3,94E-03 | 2,54E-04 | 2,93E-03 | 4,75E-04 | 2,90E-03 | 9,32E-05 |
| 8,54E+02 | 4,12E-03 | 2,56E-04 | 3,09E-03 | 4,60E-04 | 3,10E-03 | 1,05E-04 |
| 1,20E+03 | 4,36E-03 | 2,49E-04 | 3,29E-03 | 4,45E-04 | 3,35E-03 | 1,22E-04 |
| 1,67E+03 | 4,65E-03 | 2,61E-04 | 3,54E-03 | 4,43E-04 | 3,64E-03 | 1,45E-04 |
| 2,34E+03 | 5,00E-03 | 2,89E-04 | 3,81E-03 | 4,30E-04 | 3,96E-03 | 1,53E-04 |
| 3,28E+03 | 5,40E-03 | 3,19E-04 | 4,12E-03 | 4,30E-04 | 4,31E-03 | 1,71E-04 |
| 4,59E+03 | 5,85E-03 | 3,58E-04 | 4,45E-03 | 4,47E-04 | 4,70E-03 | 1,95E-04 |
| 6,43E+03 | 6,32E-03 | 4,15E-04 | 4,82E-03 | 4,51E-04 | 5,09E-03 | 2,14E-04 |
| 9,00E+03 | 6,83E-03 | 4,66E-04 | 5,21E-03 | 4,67E-04 | 5,51E-03 | 2,30E-04 |
| 1,26E+04 | 7,36E-03 | 5,29E-04 | 5,61E-03 | 4,71E-04 | 5,94E-03 | 2,45E-04 |
| 1,76E+04 | 7,91E-03 | 6,03E-04 | 6,01E-03 | 4,88E-04 | 6,37E-03 | 2,64E-04 |
| 2,47E+04 | 8,46E-03 | 6,85E-04 | 6,41E-03 | 5,11E-04 | 6,79E-03 | 2,82E-04 |
| 3,46E+04 | 9,01E-03 | 7,82E-04 | 6,80E-03 | 5,33E-04 | 7,19E-03 | 2,99E-04 |
| 4,84E+04 | 9,56E-03 | 9,02E-04 | 7,17E-03 | 5,52E-04 | 7,58E-03 | 3,11E-04 |
| 6,78E+04 | 1,01E-02 | 1,05E-03 | 7,50E-03 | 5,68E-04 | 7,93E-03 | 3,30E-04 |
| 9,49E+04 | 1,06E-02 | 1,23E-03 | 7,80E-03 | 5,87E-04 | 8,25E-03 | 3,37E-04 |
| 1,33E+05 | 1,10E-02 | 1,46E-03 | 8,07E-03 | 5,87E-04 | 8,54E-03 | 3,39E-04 |
| 1,86E+05 | 1,14E-02 | 1,83E-03 | 8,27E-03 | 5,89E-04 | 8,73E-03 | 3,60E-04 |
| 2,60E+05 | 1,19E-02 | 2,33E-03 | 8,41E-03 | 6,19E-04 | 8,89E-03 | 3,67E-04 |
| 3,64E+05 | 1,24E-02 | 3,02E-03 | 8,55E-03 | 6,28E-04 | 9,02E-03 | 3,83E-04 |
| 5,10E+05 | 1,29E-02 | 3,87E-03 | 8,65E-03 | 6,34E-04 | 9,14E-03 | 3,82E-04 |
| 7,14E+05 | 1,36E-02 | 5,02E-03 | 8,76E-03 | 6,44E-04 | 9,26E-03 | 3,97E-04 |
| 1,00E+06 | 1,42E-02 | 6,84E-03 | 8,48E-03 | 6,47E-04 | 9,00E-03 | 3,82E-04 |

| PET | 500 (h) | | 1000 (h) | | 1500 (h) | |
|----------|----------------|---------------|--------------|---------------|--------------|---------------|
| | Frequency (Hz) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) |
| 5,00E-01 | 3,99E-03 | 1,66E-03 | 3,41E-03 | 6,57E-04 | 4,22E-03 | 2,11E-03 |
| 5,21E-01 | 3,91E-03 | 1,62E-03 | 3,41E-03 | 6,15E-04 | 4,15E-03 | 2,08E-03 |
| 7,29E-01 | 3,39E-03 | 1,37E-03 | 2,89E-03 | 5,54E-04 | 3,61E-03 | 1,78E-03 |
| 1,02E+00 | 2,91E-03 | 1,12E-03 | 2,51E-03 | 4,29E-04 | 3,11E-03 | 1,43E-03 |
| 1,43E+00 | 2,57E-03 | 9,73E-04 | 2,24E-03 | 3,67E-04 | 2,81E-03 | 1,20E-03 |
| 2,00E+00 | 2,31E-03 | 8,19E-04 | 2,02E-03 | 3,13E-04 | 2,51E-03 | 9,97E-04 |
| 2,80E+00 | 2,13E-03 | 7,12E-04 | 1,88E-03 | 2,64E-04 | 2,35E-03 | 8,03E-04 |
| 3,92E+00 | 2,01E-03 | 6,53E-04 | 1,79E-03 | 2,18E-04 | 2,20E-03 | 6,92E-04 |
| 5,49E+00 | 1,92E-03 | 5,84E-04 | 1,70E-03 | 1,92E-04 | 2,12E-03 | 5,76E-04 |
| 7,68E+00 | 1,89E-03 | 5,14E-04 | 1,67E-03 | 1,63E-04 | 2,06E-03 | 5,09E-04 |
| 1,08E+01 | 1,88E-03 | 4,62E-04 | 1,68E-03 | 1,72E-04 | 2,06E-03 | 4,36E-04 |
| 1,51E+01 | 1,91E-03 | 4,30E-04 | 1,71E-03 | 1,39E-04 | 2,08E-03 | 3,93E-04 |
| 2,11E+01 | 1,97E-03 | 3,93E-04 | 1,75E-03 | 1,22E-04 | 2,12E-03 | 3,79E-04 |
| 2,95E+01 | 2,04E-03 | 3,64E-04 | 1,83E-03 | 1,23E-04 | 2,17E-03 | 3,67E-04 |
| 4,13E+01 | 2,12E-03 | 3,40E-04 | 1,91E-03 | 1,19E-04 | 2,21E-03 | 3,62E-04 |
| 5,00E+01 | 2,14E-03 | 3,32E-04 | 1,90E-03 | 1,47E-04 | 2,28E-03 | 5,06E-04 |
| 5,78E+01 | 2,20E-03 | 3,15E-04 | 1,98E-03 | 9,87E-05 | 2,28E-03 | 3,59E-04 |
| 8,10E+01 | 2,29E-03 | 2,94E-04 | 2,06E-03 | 9,72E-05 | 2,32E-03 | 3,49E-04 |
| 1,13E+02 | 2,37E-03 | 2,80E-04 | 2,13E-03 | 7,63E-05 | 2,35E-03 | 3,29E-04 |
| 1,59E+02 | 2,46E-03 | 2,60E-04 | 2,20E-03 | 6,42E-05 | 2,38E-03 | 3,07E-04 |
| 2,22E+02 | 2,56E-03 | 2,46E-04 | 2,27E-03 | 5,22E-05 | 2,42E-03 | 2,81E-04 |
| 3,11E+02 | 2,66E-03 | 2,32E-04 | 2,36E-03 | 4,66E-05 | 2,46E-03 | 2,55E-04 |
| 4,36E+02 | 2,80E-03 | 2,21E-04 | 2,46E-03 | 4,65E-05 | 2,54E-03 | 2,29E-04 |
| 6,10E+02 | 2,97E-03 | 2,08E-04 | 2,60E-03 | 5,23E-05 | 2,66E-03 | 2,07E-04 |
| 8,54E+02 | 3,17E-03 | 2,00E-04 | 2,77E-03 | 6,51E-05 | 2,81E-03 | 1,84E-04 |
| 1,20E+03 | 3,41E-03 | 1,98E-04 | 2,98E-03 | 7,97E-05 | 3,00E-03 | 1,67E-04 |
| 1,67E+03 | 3,69E-03 | 1,95E-04 | 3,22E-03 | 9,01E-05 | 3,23E-03 | 1,57E-04 |
| 2,34E+03 | 4,01E-03 | 1,97E-04 | 3,51E-03 | 1,19E-04 | 3,49E-03 | 1,53E-04 |
| 3,28E+03 | 4,36E-03 | 2,09E-04 | 3,83E-03 | 1,34E-04 | 3,80E-03 | 1,54E-04 |
| 4,59E+03 | 4,74E-03 | 2,23E-04 | 4,17E-03 | 1,60E-04 | 4,13E-03 | 1,46E-04 |
| 6,43E+03 | 5,14E-03 | 2,49E-04 | 4,55E-03 | 1,77E-04 | 4,48E-03 | 1,50E-04 |
| 9,00E+03 | 5,56E-03 | 2,60E-04 | 4,93E-03 | 1,97E-04 | 4,85E-03 | 1,57E-04 |
| 1,26E+04 | 5,99E-03 | 2,87E-04 | 5,33E-03 | 2,20E-04 | 5,24E-03 | 1,73E-04 |
| 1,76E+04 | 6,42E-03 | 3,09E-04 | 5,74E-03 | 2,39E-04 | 5,63E-03 | 1,87E-04 |
| 2,47E+04 | 6,85E-03 | 3,39E-04 | 6,15E-03 | 2,58E-04 | 6,02E-03 | 2,02E-04 |
| 3,46E+04 | 7,27E-03 | 3,62E-04 | 6,54E-03 | 2,85E-04 | 6,41E-03 | 2,19E-04 |
| 4,84E+04 | 7,66E-03 | 3,81E-04 | 6,93E-03 | 3,02E-04 | 6,79E-03 | 2,33E-04 |
| 6,78E+04 | 8,02E-03 | 4,05E-04 | 7,30E-03 | 3,19E-04 | 7,14E-03 | 2,47E-04 |
| 9,49E+04 | 8,35E-03 | 4,19E-04 | 7,63E-03 | 3,35E-04 | 7,48E-03 | 2,63E-04 |
| 1,33E+05 | 8,64E-03 | 4,32E-04 | 7,93E-03 | 3,47E-04 | 7,78E-03 | 2,84E-04 |
| 1,86E+05 | 8,85E-03 | 4,47E-04 | 8,17E-03 | 3,45E-04 | 8,04E-03 | 2,85E-04 |
| 2,60E+05 | 9,01E-03 | 4,62E-04 | 8,37E-03 | 3,54E-04 | 8,22E-03 | 3,27E-04 |
| 3,64E+05 | 9,16E-03 | 4,74E-04 | 8,55E-03 | 3,62E-04 | 8,41E-03 | 3,45E-04 |
| 5,10E+05 | 9,27E-03 | 4,78E-04 | 8,70E-03 | 3,60E-04 | 8,57E-03 | 3,78E-04 |
| 7,14E+05 | 9,40E-03 | 4,91E-04 | 8,87E-03 | 3,52E-04 | 8,74E-03 | 4,09E-04 |
| 1,00E+06 | 9,13E-03 | 5,00E-04 | 8,65E-03 | 3,66E-04 | 8,54E-03 | 4,73E-04 |

| PET | 2000 (h) | | 3000 (h) | | 4000 (h) | |
|----------|----------------|---------------|--------------|---------------|--------------|---------------|
| | Frequency (Hz) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) |
| 5,00E-01 | 6,32E-03 | 2,11E-03 | 7,34E-03 | 5,34E-03 | 2,36E-02 | 7,79E-03 |
| 5,21E-01 | 6,23E-03 | 2,11E-03 | 7,20E-03 | 5,27E-03 | 2,35E-02 | 7,77E-03 |
| 7,29E-01 | 5,34E-03 | 1,83E-03 | 6,19E-03 | 4,52E-03 | 1,98E-02 | 6,60E-03 |
| 1,02E+00 | 4,51E-03 | 1,53E-03 | 5,17E-03 | 3,66E-03 | 1,66E-02 | 5,59E-03 |
| 1,43E+00 | 3,99E-03 | 1,35E-03 | 4,54E-03 | 3,11E-03 | 1,41E-02 | 4,72E-03 |
| 2,00E+00 | 3,49E-03 | 1,18E-03 | 3,84E-03 | 2,49E-03 | 1,19E-02 | 4,02E-03 |
| 2,80E+00 | 3,15E-03 | 1,03E-03 | 3,45E-03 | 2,11E-03 | 1,03E-02 | 3,40E-03 |
| 3,92E+00 | 2,86E-03 | 9,22E-04 | 3,10E-03 | 1,79E-03 | 8,86E-03 | 2,86E-03 |
| 5,49E+00 | 2,69E-03 | 7,74E-04 | 2,85E-03 | 1,53E-03 | 7,78E-03 | 2,44E-03 |
| 7,68E+00 | 2,56E-03 | 6,89E-04 | 2,69E-03 | 1,31E-03 | 6,96E-03 | 2,08E-03 |
| 1,08E+01 | 2,47E-03 | 6,06E-04 | 2,58E-03 | 1,15E-03 | 6,32E-03 | 1,80E-03 |
| 1,51E+01 | 2,45E-03 | 5,40E-04 | 2,53E-03 | 1,04E-03 | 5,90E-03 | 1,61E-03 |
| 2,11E+01 | 2,46E-03 | 4,92E-04 | 2,53E-03 | 9,49E-04 | 5,64E-03 | 1,44E-03 |
| 2,95E+01 | 2,48E-03 | 4,48E-04 | 2,55E-03 | 8,86E-04 | 5,48E-03 | 1,31E-03 |
| 4,13E+01 | 2,54E-03 | 4,06E-04 | 2,60E-03 | 8,43E-04 | 5,44E-03 | 1,22E-03 |
| 5,00E+01 | 2,48E-03 | 5,07E-04 | 2,62E-03 | 8,42E-04 | 5,44E-03 | 1,19E-03 |
| 5,78E+01 | 2,60E-03 | 3,76E-04 | 2,66E-03 | 8,09E-04 | 5,46E-03 | 1,16E-03 |
| 8,10E+01 | 2,64E-03 | 3,57E-04 | 2,73E-03 | 7,75E-04 | 5,51E-03 | 1,12E-03 |
| 1,13E+02 | 2,71E-03 | 2,90E-04 | 2,80E-03 | 7,45E-04 | 5,54E-03 | 1,07E-03 |
| 1,59E+02 | 2,75E-03 | 2,87E-04 | 2,86E-03 | 7,02E-04 | 5,54E-03 | 1,02E-03 |
| 2,22E+02 | 2,79E-03 | 2,67E-04 | 2,92E-03 | 6,55E-04 | 5,48E-03 | 9,45E-04 |
| 3,11E+02 | 2,83E-03 | 2,55E-04 | 2,99E-03 | 6,03E-04 | 5,35E-03 | 8,61E-04 |
| 4,36E+02 | 2,89E-03 | 2,64E-04 | 3,09E-03 | 5,46E-04 | 5,19E-03 | 7,66E-04 |
| 6,10E+02 | 2,98E-03 | 2,78E-04 | 3,21E-03 | 4,92E-04 | 5,04E-03 | 6,70E-04 |
| 8,54E+02 | 3,11E-03 | 3,00E-04 | 3,37E-03 | 4,45E-04 | 4,92E-03 | 5,76E-04 |
| 1,20E+03 | 3,28E-03 | 3,28E-04 | 3,57E-03 | 4,06E-04 | 4,87E-03 | 4,89E-04 |
| 1,67E+03 | 3,50E-03 | 3,60E-04 | 3,81E-03 | 3,77E-04 | 4,88E-03 | 4,07E-04 |
| 2,34E+03 | 3,74E-03 | 3,78E-04 | 4,07E-03 | 3,58E-04 | 4,98E-03 | 3,23E-04 |
| 3,28E+03 | 4,02E-03 | 4,10E-04 | 4,39E-03 | 3,58E-04 | 5,14E-03 | 2,68E-04 |
| 4,59E+03 | 4,34E-03 | 4,47E-04 | 4,73E-03 | 3,70E-04 | 5,36E-03 | 2,11E-04 |
| 6,43E+03 | 4,67E-03 | 4,82E-04 | 5,10E-03 | 3,84E-04 | 5,66E-03 | 1,70E-04 |
| 9,00E+03 | 5,04E-03 | 5,08E-04 | 5,50E-03 | 4,04E-04 | 6,00E-03 | 1,38E-04 |
| 1,26E+04 | 5,41E-03 | 5,43E-04 | 5,90E-03 | 4,28E-04 | 6,38E-03 | 1,18E-04 |
| 1,76E+04 | 5,79E-03 | 5,76E-04 | 6,32E-03 | 4,52E-04 | 6,79E-03 | 1,05E-04 |
| 2,47E+04 | 6,17E-03 | 6,12E-04 | 6,73E-03 | 4,78E-04 | 7,22E-03 | 1,01E-04 |
| 3,46E+04 | 6,55E-03 | 6,46E-04 | 7,14E-03 | 5,07E-04 | 7,66E-03 | 9,33E-05 |
| 4,84E+04 | 6,92E-03 | 6,76E-04 | 7,53E-03 | 5,35E-04 | 8,09E-03 | 9,67E-05 |
| 6,78E+04 | 7,27E-03 | 7,06E-04 | 7,90E-03 | 5,68E-04 | 8,52E-03 | 9,57E-05 |
| 9,49E+04 | 7,60E-03 | 7,27E-04 | 8,24E-03 | 6,02E-04 | 8,92E-03 | 9,27E-05 |
| 1,33E+05 | 7,89E-03 | 7,49E-04 | 8,54E-03 | 6,36E-04 | 9,30E-03 | 9,32E-05 |
| 1,86E+05 | 8,13E-03 | 7,61E-04 | 8,76E-03 | 6,66E-04 | 9,61E-03 | 8,24E-05 |
| 2,60E+05 | 8,32E-03 | 7,97E-04 | 8,96E-03 | 7,09E-04 | 9,90E-03 | 9,38E-05 |
| 3,64E+05 | 8,49E-03 | 8,01E-04 | 9,14E-03 | 7,44E-04 | 1,02E-02 | 9,25E-05 |
| 5,10E+05 | 8,64E-03 | 8,15E-04 | 9,28E-03 | 7,78E-04 | 1,04E-02 | 9,45E-05 |
| 7,14E+05 | 8,78E-03 | 8,27E-04 | 9,43E-03 | 8,06E-04 | 1,06E-02 | 9,55E-05 |
| 1,00E+06 | 8,56E-03 | 8,25E-04 | 9,19E-03 | 8,31E-04 | 1,04E-02 | 9,89E-05 |

Attachment D – Dielectric properties in frequency range test results (PEN)

| PEN | 0 (h) | | 150 (h) | | 300 (h) | |
|----------|---------------|--------------|---------------|--------------|---------------|--------------|
| | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) |
| 5,00E-01 | 9,12E-03 | 4,42E-03 | 1,40E-02 | 9,82E-03 | 1,19E-02 | 3,25E-03 |
| 5,21E-01 | 9,12E-03 | 4,34E-03 | 1,41E-02 | 9,44E-03 | 1,17E-02 | 3,13E-03 |
| 7,29E-01 | 8,23E-03 | 3,77E-03 | 1,26E-02 | 8,34E-03 | 1,02E-02 | 2,61E-03 |
| 1,02E+00 | 7,31E-03 | 3,03E-03 | 1,10E-02 | 6,83E-03 | 8,99E-03 | 1,97E-03 |
| 1,43E+00 | 6,64E-03 | 2,56E-03 | 9,79E-03 | 5,86E-03 | 7,87E-03 | 1,63E-03 |
| 2,00E+00 | 5,99E-03 | 2,04E-03 | 8,67E-03 | 4,71E-03 | 7,06E-03 | 1,36E-03 |
| 2,80E+00 | 5,59E-03 | 1,69E-03 | 7,91E-03 | 3,92E-03 | 6,53E-03 | 1,08E-03 |
| 3,92E+00 | 5,20E-03 | 1,41E-03 | 7,21E-03 | 3,24E-03 | 6,00E-03 | 8,95E-04 |
| 5,49E+00 | 4,90E-03 | 1,18E-03 | 6,66E-03 | 2,65E-03 | 5,63E-03 | 7,48E-04 |
| 7,68E+00 | 4,66E-03 | 9,70E-04 | 6,24E-03 | 2,14E-03 | 5,37E-03 | 6,52E-04 |
| 1,08E+01 | 4,48E-03 | 8,15E-04 | 5,93E-03 | 1,74E-03 | 5,18E-03 | 5,85E-04 |
| 1,51E+01 | 4,36E-03 | 7,06E-04 | 5,69E-03 | 1,41E-03 | 5,05E-03 | 5,41E-04 |
| 2,11E+01 | 4,28E-03 | 6,24E-04 | 5,52E-03 | 1,17E-03 | 4,96E-03 | 5,08E-04 |
| 2,95E+01 | 4,23E-03 | 5,71E-04 | 5,38E-03 | 9,79E-04 | 4,90E-03 | 5,02E-04 |
| 4,13E+01 | 4,20E-03 | 5,40E-04 | 5,28E-03 | 8,32E-04 | 4,83E-03 | 4,98E-04 |
| 5,00E+01 | 4,28E-03 | 5,12E-04 | 5,22E-03 | 7,78E-04 | 4,82E-03 | 4,30E-04 |
| 5,78E+01 | 4,22E-03 | 5,17E-04 | 5,17E-03 | 7,42E-04 | 4,77E-03 | 4,94E-04 |
| 8,10E+01 | 4,18E-03 | 5,01E-04 | 5,05E-03 | 6,85E-04 | 4,68E-03 | 4,85E-04 |
| 1,13E+02 | 4,16E-03 | 4,69E-04 | 4,92E-03 | 6,57E-04 | 4,58E-03 | 4,85E-04 |
| 1,59E+02 | 4,11E-03 | 4,45E-04 | 4,76E-03 | 6,48E-04 | 4,42E-03 | 4,82E-04 |
| 2,22E+02 | 4,07E-03 | 4,15E-04 | 4,58E-03 | 6,57E-04 | 4,26E-03 | 4,67E-04 |
| 3,11E+02 | 4,01E-03 | 3,73E-04 | 4,40E-03 | 6,65E-04 | 4,07E-03 | 4,53E-04 |
| 4,36E+02 | 3,95E-03 | 3,34E-04 | 4,22E-03 | 6,78E-04 | 3,89E-03 | 4,35E-04 |
| 6,10E+02 | 3,90E-03 | 3,01E-04 | 4,06E-03 | 6,73E-04 | 3,73E-03 | 4,21E-04 |
| 8,54E+02 | 3,88E-03 | 2,75E-04 | 3,94E-03 | 6,54E-04 | 3,59E-03 | 4,06E-04 |
| 1,20E+03 | 3,88E-03 | 2,57E-04 | 3,86E-03 | 6,26E-04 | 3,49E-03 | 4,01E-04 |
| 1,67E+03 | 3,92E-03 | 2,37E-04 | 3,81E-03 | 5,89E-04 | 3,43E-03 | 3,93E-04 |
| 2,34E+03 | 3,99E-03 | 2,36E-04 | 3,81E-03 | 5,39E-04 | 3,41E-03 | 4,14E-04 |
| 3,28E+03 | 4,10E-03 | 2,22E-04 | 3,85E-03 | 4,96E-04 | 3,43E-03 | 4,17E-04 |
| 4,59E+03 | 4,25E-03 | 2,27E-04 | 3,92E-03 | 4,51E-04 | 3,48E-03 | 4,46E-04 |
| 6,43E+03 | 4,43E-03 | 2,20E-04 | 4,01E-03 | 4,22E-04 | 3,55E-03 | 4,78E-04 |
| 9,00E+03 | 4,62E-03 | 2,31E-04 | 4,14E-03 | 4,02E-04 | 3,64E-03 | 5,19E-04 |
| 1,26E+04 | 4,83E-03 | 2,33E-04 | 4,27E-03 | 3,89E-04 | 3,75E-03 | 5,46E-04 |
| 1,76E+04 | 5,04E-03 | 2,46E-04 | 4,40E-03 | 3,80E-04 | 3,85E-03 | 5,80E-04 |
| 2,47E+04 | 5,24E-03 | 2,45E-04 | 4,53E-03 | 3,76E-04 | 3,96E-03 | 6,07E-04 |
| 3,46E+04 | 5,43E-03 | 2,59E-04 | 4,65E-03 | 3,77E-04 | 4,07E-03 | 6,12E-04 |
| 4,84E+04 | 5,59E-03 | 2,70E-04 | 4,75E-03 | 3,74E-04 | 4,16E-03 | 6,09E-04 |
| 6,78E+04 | 5,73E-03 | 2,80E-04 | 4,84E-03 | 3,78E-04 | 4,25E-03 | 5,97E-04 |
| 9,49E+04 | 5,85E-03 | 2,86E-04 | 4,89E-03 | 3,73E-04 | 4,31E-03 | 5,80E-04 |
| 1,33E+05 | 5,90E-03 | 2,91E-04 | 4,92E-03 | 3,52E-04 | 4,35E-03 | 5,64E-04 |
| 1,86E+05 | 5,96E-03 | 3,00E-04 | 4,92E-03 | 3,50E-04 | 4,34E-03 | 5,40E-04 |
| 2,60E+05 | 6,01E-03 | 2,93E-04 | 4,91E-03 | 3,49E-04 | 4,33E-03 | 5,43E-04 |
| 3,64E+05 | 6,04E-03 | 2,99E-04 | 4,90E-03 | 3,46E-04 | 4,32E-03 | 5,38E-04 |
| 5,10E+05 | 6,07E-03 | 3,05E-04 | 4,90E-03 | 3,39E-04 | 4,30E-03 | 5,41E-04 |
| 7,14E+05 | 6,14E-03 | 3,10E-04 | 4,94E-03 | 3,35E-04 | 4,33E-03 | 5,50E-04 |
| 1,00E+06 | 5,88E-03 | 3,08E-04 | 4,61E-03 | 3,27E-04 | 4,00E-03 | 5,26E-04 |

| PEN | 500 (h) | | 1000 (h) | | 1500 (h) | |
|----------|---------------|--------------|---------------|--------------|---------------|--------------|
| | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) |
| 5,00E-01 | 1,48E-02 | 6,09E-03 | 1,41E-02 | 1,20E-02 | 1,59E-02 | 3,62E-03 |
| 5,21E-01 | 1,45E-02 | 5,97E-03 | 1,40E-02 | 1,21E-02 | 1,57E-02 | 3,60E-03 |
| 7,29E-01 | 1,27E-02 | 5,16E-03 | 1,28E-02 | 1,15E-02 | 1,37E-02 | 3,17E-03 |
| 1,02E+00 | 1,10E-02 | 3,88E-03 | 1,17E-02 | 1,05E-02 | 1,18E-02 | 2,60E-03 |
| 1,43E+00 | 9,77E-03 | 3,13E-03 | 1,08E-02 | 9,70E-03 | 1,04E-02 | 2,20E-03 |
| 2,00E+00 | 8,63E-03 | 3,18E-03 | 9,51E-03 | 8,51E-03 | 9,27E-03 | 1,84E-03 |
| 2,80E+00 | 7,61E-03 | 2,40E-03 | 8,80E-03 | 7,53E-03 | 8,50E-03 | 1,62E-03 |
| 3,92E+00 | 6,93E-03 | 1,98E-03 | 8,04E-03 | 6,59E-03 | 7,69E-03 | 1,34E-03 |
| 5,49E+00 | 6,42E-03 | 1,70E-03 | 7,40E-03 | 5,70E-03 | 7,13E-03 | 1,15E-03 |
| 7,68E+00 | 6,07E-03 | 1,48E-03 | 6,90E-03 | 4,92E-03 | 6,74E-03 | 9,97E-04 |
| 1,08E+01 | 5,79E-03 | 1,30E-03 | 6,43E-03 | 4,15E-03 | 6,38E-03 | 8,57E-04 |
| 1,51E+01 | 5,60E-03 | 1,16E-03 | 6,07E-03 | 3,57E-03 | 6,11E-03 | 7,75E-04 |
| 2,11E+01 | 5,46E-03 | 1,05E-03 | 5,77E-03 | 3,07E-03 | 5,90E-03 | 7,02E-04 |
| 2,95E+01 | 5,36E-03 | 9,83E-04 | 5,52E-03 | 2,68E-03 | 5,71E-03 | 6,49E-04 |
| 4,13E+01 | 5,27E-03 | 9,33E-04 | 5,29E-03 | 2,37E-03 | 5,53E-03 | 6,07E-04 |
| 5,00E+01 | 5,22E-03 | 8,76E-04 | 5,19E-03 | 2,22E-03 | 5,43E-03 | 5,65E-04 |
| 5,78E+01 | 5,17E-03 | 8,97E-04 | 5,07E-03 | 2,13E-03 | 5,33E-03 | 5,67E-04 |
| 8,10E+01 | 5,04E-03 | 8,55E-04 | 4,86E-03 | 1,94E-03 | 5,10E-03 | 5,35E-04 |
| 1,13E+02 | 4,88E-03 | 8,08E-04 | 4,63E-03 | 1,78E-03 | 4,84E-03 | 5,00E-04 |
| 1,59E+02 | 4,67E-03 | 7,54E-04 | 4,39E-03 | 1,64E-03 | 4,55E-03 | 4,84E-04 |
| 2,22E+02 | 4,43E-03 | 6,88E-04 | 4,16E-03 | 1,52E-03 | 4,25E-03 | 4,66E-04 |
| 3,11E+02 | 4,18E-03 | 6,15E-04 | 3,94E-03 | 1,39E-03 | 3,96E-03 | 4,56E-04 |
| 4,36E+02 | 3,94E-03 | 5,41E-04 | 3,73E-03 | 1,28E-03 | 3,71E-03 | 4,45E-04 |
| 6,10E+02 | 3,73E-03 | 4,69E-04 | 3,57E-03 | 1,17E-03 | 3,49E-03 | 4,46E-04 |
| 8,54E+02 | 3,57E-03 | 4,05E-04 | 3,43E-03 | 1,07E-03 | 3,34E-03 | 4,38E-04 |
| 1,20E+03 | 3,47E-03 | 3,53E-04 | 3,35E-03 | 9,82E-04 | 3,24E-03 | 4,29E-04 |
| 1,67E+03 | 3,41E-03 | 2,96E-04 | 3,31E-03 | 8,89E-04 | 3,18E-03 | 4,27E-04 |
| 2,34E+03 | 3,39E-03 | 2,63E-04 | 3,29E-03 | 7,98E-04 | 3,16E-03 | 4,16E-04 |
| 3,28E+03 | 3,42E-03 | 2,32E-04 | 3,31E-03 | 7,22E-04 | 3,18E-03 | 4,18E-04 |
| 4,59E+03 | 3,49E-03 | 2,11E-04 | 3,36E-03 | 6,59E-04 | 3,23E-03 | 4,16E-04 |
| 6,43E+03 | 3,58E-03 | 1,98E-04 | 3,43E-03 | 6,04E-04 | 3,30E-03 | 4,26E-04 |
| 9,00E+03 | 3,68E-03 | 1,90E-04 | 3,53E-03 | 5,77E-04 | 3,40E-03 | 4,34E-04 |
| 1,26E+04 | 3,81E-03 | 1,83E-04 | 3,64E-03 | 5,50E-04 | 3,51E-03 | 4,45E-04 |
| 1,76E+04 | 3,93E-03 | 1,81E-04 | 3,75E-03 | 5,31E-04 | 3,61E-03 | 4,57E-04 |
| 2,47E+04 | 4,05E-03 | 1,77E-04 | 3,87E-03 | 5,22E-04 | 3,71E-03 | 4,63E-04 |
| 3,46E+04 | 4,16E-03 | 1,92E-04 | 3,96E-03 | 5,20E-04 | 3,81E-03 | 4,73E-04 |
| 4,84E+04 | 4,25E-03 | 1,94E-04 | 4,05E-03 | 5,31E-04 | 3,91E-03 | 4,88E-04 |
| 6,78E+04 | 4,34E-03 | 2,04E-04 | 4,14E-03 | 5,27E-04 | 3,98E-03 | 5,05E-04 |
| 9,49E+04 | 4,40E-03 | 2,09E-04 | 4,20E-03 | 5,29E-04 | 4,03E-03 | 5,03E-04 |
| 1,33E+05 | 4,43E-03 | 2,01E-04 | 4,25E-03 | 5,26E-04 | 4,07E-03 | 5,06E-04 |
| 1,86E+05 | 4,43E-03 | 2,14E-04 | 4,24E-03 | 5,15E-04 | 4,07E-03 | 4,92E-04 |
| 2,60E+05 | 4,43E-03 | 2,32E-04 | 4,23E-03 | 5,35E-04 | 4,06E-03 | 5,19E-04 |
| 3,64E+05 | 4,42E-03 | 2,35E-04 | 4,23E-03 | 5,37E-04 | 4,05E-03 | 5,24E-04 |
| 5,10E+05 | 4,42E-03 | 2,42E-04 | 4,22E-03 | 5,49E-04 | 4,05E-03 | 5,33E-04 |
| 7,14E+05 | 4,46E-03 | 2,54E-04 | 4,25E-03 | 5,67E-04 | 4,08E-03 | 5,62E-04 |
| 1,00E+06 | 4,14E-03 | 2,63E-04 | 3,92E-03 | 5,87E-04 | 3,76E-03 | 5,83E-04 |

| PEN | 2000 (h) | | 3000 (h) | | 4000 (h) | |
|----------|---------------|--------------|---------------|--------------|---------------|--------------|
| | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) | tgδ aver. (-) | st. dev. (-) |
| 5,00E-01 | 1,92E-02 | 1,01E-02 | 1,92E-02 | 8,00E-03 | 2,29E-02 | 9,04E-03 |
| 5,21E-01 | 1,89E-02 | 9,99E-03 | 1,90E-02 | 8,00E-03 | 2,26E-02 | 8,89E-03 |
| 7,29E-01 | 1,65E-02 | 8,71E-03 | 1,68E-02 | 6,97E-03 | 2,02E-02 | 8,01E-03 |
| 1,02E+00 | 1,40E-02 | 7,16E-03 | 1,46E-02 | 5,88E-03 | 1,78E-02 | 7,11E-03 |
| 1,43E+00 | 1,24E-02 | 6,01E-03 | 1,30E-02 | 5,07E-03 | 1,59E-02 | 6,37E-03 |
| 2,00E+00 | 1,09E-02 | 4,89E-03 | 1,16E-02 | 4,27E-03 | 1,44E-02 | 5,73E-03 |
| 2,80E+00 | 9,91E-03 | 4,16E-03 | 1,06E-02 | 3,72E-03 | 1,31E-02 | 5,22E-03 |
| 3,92E+00 | 8,99E-03 | 3,48E-03 | 9,69E-03 | 3,23E-03 | 1,19E-02 | 4,68E-03 |
| 5,49E+00 | 8,32E-03 | 2,92E-03 | 8,98E-03 | 2,78E-03 | 1,10E-02 | 4,25E-03 |
| 7,68E+00 | 7,82E-03 | 2,51E-03 | 8,40E-03 | 2,44E-03 | 1,03E-02 | 3,90E-03 |
| 1,08E+01 | 7,42E-03 | 2,21E-03 | 7,91E-03 | 2,11E-03 | 9,59E-03 | 3,57E-03 |
| 1,51E+01 | 7,13E-03 | 1,99E-03 | 7,51E-03 | 1,87E-03 | 9,09E-03 | 3,34E-03 |
| 2,11E+01 | 6,88E-03 | 1,82E-03 | 7,17E-03 | 1,68E-03 | 8,67E-03 | 3,11E-03 |
| 2,95E+01 | 6,66E-03 | 1,68E-03 | 6,85E-03 | 1,52E-03 | 8,28E-03 | 2,92E-03 |
| 4,13E+01 | 6,46E-03 | 1,55E-03 | 6,53E-03 | 1,37E-03 | 7,96E-03 | 2,76E-03 |
| 5,00E+01 | 6,31E-03 | 1,48E-03 | 6,37E-03 | 1,27E-03 | 7,75E-03 | 2,67E-03 |
| 5,78E+01 | 6,23E-03 | 1,44E-03 | 6,19E-03 | 1,23E-03 | 7,63E-03 | 2,60E-03 |
| 8,10E+01 | 5,96E-03 | 1,31E-03 | 5,83E-03 | 1,09E-03 | 7,34E-03 | 2,48E-03 |
| 1,13E+02 | 5,64E-03 | 1,19E-03 | 5,45E-03 | 9,47E-04 | 7,04E-03 | 2,36E-03 |
| 1,59E+02 | 5,29E-03 | 1,08E-03 | 5,05E-03 | 8,10E-04 | 6,73E-03 | 2,23E-03 |
| 2,22E+02 | 4,91E-03 | 9,75E-04 | 4,67E-03 | 6,82E-04 | 6,41E-03 | 2,10E-03 |
| 3,11E+02 | 4,54E-03 | 8,92E-04 | 4,33E-03 | 5,69E-04 | 6,07E-03 | 1,97E-03 |
| 4,36E+02 | 4,21E-03 | 8,18E-04 | 4,04E-03 | 4,76E-04 | 5,74E-03 | 1,83E-03 |
| 6,10E+02 | 3,93E-03 | 7,51E-04 | 3,81E-03 | 4,03E-04 | 5,40E-03 | 1,68E-03 |
| 8,54E+02 | 3,71E-03 | 6,88E-04 | 3,64E-03 | 3,47E-04 | 5,08E-03 | 1,54E-03 |
| 1,20E+03 | 3,56E-03 | 6,30E-04 | 3,53E-03 | 3,09E-04 | 4,79E-03 | 1,40E-03 |
| 1,67E+03 | 3,46E-03 | 5,77E-04 | 3,46E-03 | 2,87E-04 | 4,54E-03 | 1,26E-03 |
| 2,34E+03 | 3,40E-03 | 5,32E-04 | 3,45E-03 | 2,65E-04 | 4,33E-03 | 1,13E-03 |
| 3,28E+03 | 3,39E-03 | 4,97E-04 | 3,48E-03 | 2,65E-04 | 4,17E-03 | 1,01E-03 |
| 4,59E+03 | 3,42E-03 | 4,75E-04 | 3,54E-03 | 2,50E-04 | 4,06E-03 | 9,22E-04 |
| 6,43E+03 | 3,47E-03 | 4,62E-04 | 3,62E-03 | 2,65E-04 | 4,02E-03 | 8,55E-04 |
| 9,00E+03 | 3,55E-03 | 4,51E-04 | 3,73E-03 | 2,71E-04 | 4,02E-03 | 8,00E-04 |
| 1,26E+04 | 3,63E-03 | 4,49E-04 | 3,84E-03 | 2,83E-04 | 4,06E-03 | 7,70E-04 |
| 1,76E+04 | 3,74E-03 | 4,56E-04 | 3,96E-03 | 2,95E-04 | 4,13E-03 | 7,52E-04 |
| 2,47E+04 | 3,83E-03 | 4,65E-04 | 4,09E-03 | 3,13E-04 | 4,22E-03 | 7,50E-04 |
| 3,46E+04 | 3,92E-03 | 4,75E-04 | 4,20E-03 | 3,31E-04 | 4,32E-03 | 7,57E-04 |
| 4,84E+04 | 4,01E-03 | 4,78E-04 | 4,31E-03 | 3,44E-04 | 4,43E-03 | 7,66E-04 |
| 6,78E+04 | 4,07E-03 | 4,90E-04 | 4,40E-03 | 3,57E-04 | 4,52E-03 | 7,79E-04 |
| 9,49E+04 | 4,12E-03 | 4,98E-04 | 4,46E-03 | 3,72E-04 | 4,60E-03 | 7,97E-04 |
| 1,33E+05 | 4,16E-03 | 4,83E-04 | 4,52E-03 | 3,89E-04 | 4,66E-03 | 8,06E-04 |
| 1,86E+05 | 4,14E-03 | 5,08E-04 | 4,51E-03 | 3,91E-04 | 4,68E-03 | 8,07E-04 |
| 2,60E+05 | 4,15E-03 | 5,13E-04 | 4,53E-03 | 4,07E-04 | 4,69E-03 | 8,31E-04 |
| 3,64E+05 | 4,15E-03 | 5,20E-04 | 4,53E-03 | 4,15E-04 | 4,68E-03 | 8,42E-04 |
| 5,10E+05 | 4,15E-03 | 5,26E-04 | 4,54E-03 | 4,22E-04 | 4,69E-03 | 8,59E-04 |
| 7,14E+05 | 4,18E-03 | 5,47E-04 | 4,57E-03 | 4,36E-04 | 4,73E-03 | 8,97E-04 |
| 1,00E+06 | 3,87E-03 | 5,59E-04 | 4,26E-03 | 4,43E-04 | 4,40E-03 | 9,04E-04 |