TECHNICAL UNIVERSITY OF LIBEREC

FACULTY OF MECHANICAL ENGINEERING

DEPARTMENT OF MATERIAL SCIENCE

DIPLOMA THESIS

2004   **FAHAD AL-SARAWI**

TECHNICAL UNIVERSITY OF LIBEREC

FACULTY OF MECHANICAL ENGINEERING

DEPARTMENT OF MATERIAL SCIENCE

STUDY PROGRAM: M2301
MECHANICAL ENGINEERING

DISCIPLINE: 2303 T 002
ENGINEERING TECHNOLOGY

DIRECTION:
MATERIAL ENGINEERING

POLYMER COMPOSITES: INFLUENCE OF THE SHAPE

AND SIZE OF THE FILLER ON   SELECTED PROPERTIES

NUMBER OF THESIS:
KMT – 193

FAHAD AL-SARAWI

Supervisor: Doc. RNDr. František Lednický, CSc.
Consultant: Ing . Dora Kroisová, Ph.D.

RANGE OF DIPLOMA THESIS:
Number of pages: 55
Number of tables: 4
Number of figures: 35

TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Mechanical Engineering

Department of Material Science   Study year: 2003/04

THEME OF DIPLOMA THESIS

Name and Surname   **Fahad ALSARAWI**

Study program   **M2301 Mechanical Engineering**

Discipline   **2303 T 002 Engineering Technology**

Direction   **Material Engineering**

According to Act No. 111/1998 Sb. on Higher Education Institutions you have recieved diploma work with theme:

Polymer composites: influence of the shape and size of the filler on selected properties

Instructions for elaboration:
(List principal goals and recommended methods for elaboration of the master thesis)

1. Study the behaviour of filled polymer composite systems.
2. Prepare samples of polymer composites with a silicone matrix and with fillers based on silicone dioxide. Study the influence of the shape and size of these fillers on some selected parameters (mechanical – a particularly strength, Young modulus; swelling). Document microscopically size and shape of the particles, and the particle distribution from fracture surfaces. Describe the experimental techniques used.
3. Describe and discuss the results obtained.
4. Formulate conclusions.

KMT/MI
$55 s.$
$tab., obr.$

$V75/04S$

Elaboration form of the diploma work:

- report with extent from 30 to 40 pages
- attachements and/or appendices

List of literature (Cite recommended professional literature):

[1] Hull D., An introduction to composite materials, Cambridge, 1990.

[2] Engineered Materials Handbook, Volume 2: Engineering Plastics (Epel J.N., Margolis J.M., Newman S., Seymour R.B., Eds.), ASM International, 2000.

[3]Clarson S.J., Mark J.E., Silicone elastomers, in: The Polymeric Materials Encyclopedia, CRC Press, Inc., 1996.

Supervisor: Doc.RNDr. František Lednický, CSc.
Consultant: Ing. Dora Kroisová, Ph.D.

L.S.

prof. RNDr. Petr ŠPATENKA,CSc.
Head of the Department

doc. Ing. Petr LOUDA, CSc.
Dean

Liberec on 31.10. 2003

The theme of master thesis is valid 15 months the from abovementioned date. Terms for delivery of master work are determined and published in the time schedule of education for the each study year.

<u>ANNOTATION</u>

NAME: FAHAD AL-SARAWI

STUDY PROGRAM: M2301 - MECHANICAL ENGINEERING

DISCIPLINE: 2303 T 002 - ENGINEERING TECHNOLOGY

DIRECTION: MATERIAL ENGINEERING

THEME OF DIPLOMA THESIS: POLYMER COMPOSITES: INFLUENCE OF THE SHAPE AND SIZE OF THE FILLER ON SELECTED PROPERTIES

NUMBER OF THESIS: KMT – 193

SUPERVISOR: Doc. RNDr. FRANTIŠEK LEDNICKÝ, CsC.

CONSULTANT: Ing. DORA KROISOVÁ, Ph.D.

Study of mechanical properties of the polysiloxane (silicone rubber) filled with selected inorganic filler, and connection with its phase structure and swelling properties was the object of this study.

Introduction deals with structure-properties relationship in general. Materials and methods are described in the second part: polymer matrix and fillers characterisation, stress-strain measurements, soft matrix fracture surface technique, sample preparation for microscopy, and measurement of swelling kinetics. Results of the mechanical measurements, microscopical characterisation, and swelling kinetic results are presented and discussed in the following chapter.

Six types of filler were selected (fumed and precipitated silicon dioxide, glass flakes, glass bubbles, quartz sand, and montmorillonite) in weight concentrations up to 8 parts per hundred of the rubber content were added to matrix. Tensile strength, modulus, and extensibility of the systems were measured and compared with the filler distribution in the sample (aggregation, sedimentation, interfacial adhesion), and with the swelling kinetics.

Fumed silicon dioxide proved to be the best, and quartz sand the worst filler from the six selected, as far as the used points of view are concerned. Chemical similarity of the filler, interfacial adhesion, particle size, particle aggregation, and particle sedimentation and their influence on the mechanical parameters and on the swelling behaviour were discussed.

TECHNICKÁ UNIVERZITA V LIBERCI

FAKULTA STROJNÍ

KATEDRA MATERIÁLU

Hálkova 6, 461 18 Liberec

Telefon: 420 485 353 116, fax: 420 485 353 342

ANOTACE

JMÉNO: FAHAD AL-SARAWI

STUDIJNÍ PROGRAM: M2301 - STROJNÍ INŽENÝRSTVÍ

OBOR: 2303 T 002 - STROJÍRENSKÁ TECHNOLOGIE

ZAMĚŘENÍ: MATERIÁLOVÉ INŽENÝRSTVÍ

NÁZEV DIPLOMOVÉ PRÁCE: POLYMERNÍ KOMPOZITY: VLIV TVARU A VELIKOSTI PLNIVA NA VYBRANÉ VLASTNOSTI

ČÍSLO PRÁCE: KMT – 193

VEDOUCÍ DIPLOMOVÉ PRÁCE: Doc. RNDr. FRANTIŠEK LEDNICKÝ, CsC.

KONZULTANT: Ing. DORA KROISOVÁ, Ph.D.

Předmětem diplomové práce je studium mechanických vlastností polysiloxanů (silikonových kaučuků) plněných vybranými anorganickými plnivy v souvislosti s jejich fázovou strukturou a procesem botnání.

Úvodní část se zabývá obecně problematikou vztahu struktury a vlastností materiálu. Materiály a metody jsou popsány ve druhé části práce: matrice, plniva a jejich charakteristika, měření závislosti napětí a deformace, technika přípravy lomových ploch vzorků z měkkých polymerů, preparace vzorků pro mikroskopické hodnocení, měření procesu botnání. Výsledky mechanických měření, mikroskopického pozorování a procesu botnání jsou prezentovány a diskutovány v následující kapitole.

Bylo vybráno 6 typů plniv (pyrogenní a srážený oxid křemičitý, skleněné mikrodestičky, skleněné duté kuličky, křemenný písek a montmorillonit), které byly přidávány do matrice

v množstvích do 8 phr. Byly stanoveny meze pevnosti v tahu, moduly pružnosti a prodloužení, které byly porovnávány s distribucí plniva ve vzorku (agregací, sedimentací, mezifázovou adhezí) a s procesem botnání.

Ze šesti vybraných plniv se pyrogenní amorfní oxid křemičitý jeví jako nejlepší, křemenný písek naopak jako nejhorší plnivo. Chemická podobnost plniv, mezifázová adheze, velikost, agregace a sedimentace částic a jejich vliv na mechanické parametry a botnání jsou zde diskutovány.

KLÍČOVÁ SLOVA

Polysiloxany, silikonový kaučuk, plněné polymery, plniva, mechanické vlastnosti, zkouška tahem, mez pevnosti v tahu, modul pružnosti, prodloužení, fázová struktura, lomové plochy, process botnání.

ACKNOWLEDGEMENTS

I assert that I have worked out my diploma thesis alone and that I have used only literature, which is given as references. I acknowledge the corrections of text made by the diploma leaders. I agree with lending this thesis for educational or research purpose.

May 25, 2004   FAHAD AL-SARAWI

CONTENTS

1 INTRODUCTION

1.0 HISTORY OF POLYMERS

The simplest definition of a polymer is something made of many units. We can think of a polymer molecule as a chain. Each link of the chain is the "mer" or basic unit. Mers can be made of atoms of carbon and hydrogen while other mers may also include atoms of oxygen or nitrogen. Some mers are made of silicon and oxygen. To make the chain, many links or "mers" are hooked or polymerized together. Polymerization can be demonstrated by linking strips of construction paper together to make paper garlands or hooking together hundreds of paper clips to form chains.

Polymers have been with us since the beginning of time. Natural polymers include such things as tar and shellac, tortoise shell and horns, as well as tree saps that produce amber and latex. These polymers were processed with heat and pressure into useful articles like hair ornaments and jewellery. Natural polymers began to be chemically modified during the 1800s to produce many materials. The most famous of these were vulcanized rubber, gun cotton, and celluloid. The first synthetic polymer produced was Bakelite in 1909 and was soon followed by the first semi- synthetic fibre, rayon, which was developed in 1911.

Even with these developments, it was not until World War II that significant changes took place in the polymer industry. Prior to World War II, natural substances were generally available; therefore, synthetics that were being developed were not a necessity. Once the world went to war, our natural sources of latex, wool, silk, and other materials were cut off, making the use of synthetics critical. During this time period, we saw the use of nylon, acrylic, neoprene, SBR, polyethylene, and many more polymers take the place of natural materials that were scarce. Since then, the polymer industry has continued to grow and has evolved into one of the fastest growing industries in the U.S. and in the world. [1]

1.1 GENERAL CHARACTERISTICS OF POLYMERS
1.1.1 STRUCTURE OF MACROMOLECULAR CHAINS

Polymer is a high-molecular weight (organic) compound, natural or synthetic, with a structure that can be represented by repeated small unit, the mer. Examples can include polyethylene (synthetic polymer), rubber (synthetic or natural polymer) and cellulose (natural polymer). Synthetic polymers are formed by addition or condensation polymerization of monomers. When two or more different monomers are involved in the macromolecular chain,

the product is called a copolymer. The chain lengths of commercial thermoplastics vary from about 1000 to about 100 000 repeating units. [2]

Oligomer is a compound consisting of only a few monomer units, for example – dimer, trimer, tetramer and/or their mixtures. If the number of monomer units is increased sufficiently, a polymer is obtained. [2]

Monomer is a single molecule that can react with like or unlike molecules to form a polymer. As an example, chemical structure of ethylene (monomer from which polyethylene is produced) is $CH_2=CH_2$. MER, the smallest repeating structure of polymer is called *monomer unit*. Chemical structure of the mer of polyethylene (PE) is $[-CH_2-CH_2-]$. [2]

Polymerization is the chemical reaction in which the molecules of a monomer are linked together (react) to form large molecules (*macromolecules*) with a molecular weight that is a multiple of the molecular weight of original substance. When two or more monomers are involved, the process is called copolymerization. [2]

Degree of polymerization is the number of structural units, or mers, in the average polymer molecule in a sample. It is a measure of molecular weight. [2]

Molecular mass (*molar mass, molecular weight*) is defined as the sum of the atomic mass of all atoms in molecule. In high polymers, because the molecular masses of individual macromolecules vary widely, they must be expressed as average. The average molecular mass of polymers may be expressed as the number average or weight average. These averages are the first two moments of the molecular mass or weight distribution. [2] Molecular mass is a measure of the chain length.

1.1.2 POLYMER CHAIN AND ITS ARCHITECTURE

Various classes of the polymer chains are in Fig 1.1 together with names of the polymer types. [3] Two kinds of mers are depicted as open and black circles respectively. Polymer chains can exhibit various architecture according to the chemical reactions during their creation. Schematic representation of the different molecular architectures are in Fig. 1.2.
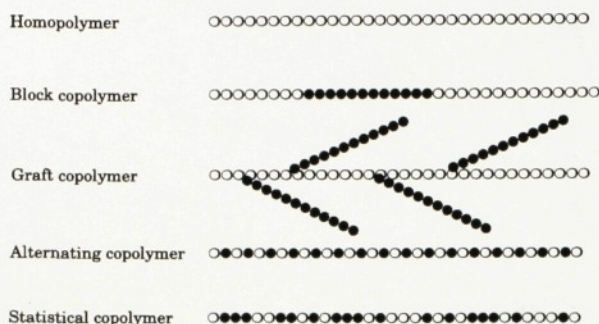
Homopolymer	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
Block copolymer	OOOOOOOO●●●●●●●●●●●●●●OOOOOOOOOOOOOOO
Graft copolymer	(figure)
Alternating copolymer	O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●O●
Statistical copolymer	O●●●OO●●O●O●●●O●OOO●O●O●O●●●O●OOO●O

Fig. 1.1 Homopolymers and different classes of copolymers. [3]

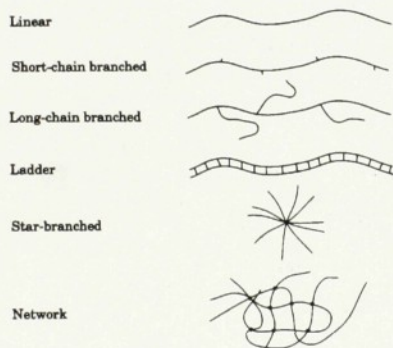| Linear | |
Short-chain branched	
Long-chain branched	
Ladder	
Star-branched	
Network	

Fig. 1.2 Schematic representation of structures of polymers with different molecular architecture. [3]

1.1.3 SUPERMOLECULAR STRUCTURES

Macroscopic properties of (polymeric) materials depend not only on their chemical nature (atomic, molecular structure) but also on the arrangement of atoms or molecules in the supermolecular level. That fact is called "hierarchy of structures". Amorphous polymers exhibit the simplest arrangement of their chains. There is no substantial order of the individual chains. The chains are coiled and entangled.

Crystalline polymers exhibit structures that are more complicated. Parts of the macromolecular chains are ordered in crystalline regions, the remaining parts are in amorphous regions. Crystalline regions are usually layered lamellar crystals formed by chain-

folded crystals. Crystalline lamellae are interchanged with amorphous regions and usually are arranged into higher-level textures called spherulites. The spherulites grow during cooling from melt in the course of the shaping of the product. Sizes of spherulites, their interconnections and population within the cross-section of the product influence very much the final properties of the material.

Polymer blends are prepared from melt of two or more polymers. Different polymers are compatible only very seldom. Therefore, the blend properties are usually improved by a compatibilizer, which can increase the interfacial adhesion of the polymer components and/or decrease the size of the dispersed particles of the minority component. Both the effects improve mechanical properties of the resulting materials.

Filled polymers are characteristic by the presence of inorganic dispersed particles in the polymer matrix. Fillers are usually less expensive and increase the Young modulus of the material and correspondingly the other properties, including dimensional stability. Interfacial adhesion is very often modified with sizing, in which the filler is treated with another component. Fillers are the particulate materials, particles of which are isometric (comparable dimensions in all directions). Fillers, particles of that exhibit a pronounced aspect ratio (ratio of the largest dimension to the smallest one is higher than about ten) are usually called reinforcing agents and the materials are called polymer composites. In polymer composites, a substantial part of mechanical loading is transferred by the reinforcing agent particles.

It is useful to divide the polymers into two main classes: the fully amorphous and the semicrystalline. The fully amorphous polymers show no sharp, crystalline Bragg reflection in the X-ray diffractograms taken at any temperature. The reason why these polymers are unable to crystallize is commonly their irregular chain structure. Atactic polymers, statistical copolymers and highly branched polymers belong to this class of polymers. The semicrystalline polymers show crystalline Bragg reflections superimposed on an amorphous background. Thus, they always consist of two components differing in degree of order: a crystalline component composed of thin (about 10 nm) lamella-shaped crystals and an amorphous component. The degree of crystallinity can be as high as 90 % for certain low-molar-mass polyethylenes and as low as 5 % for poly(vinyl chloride).

A third, recently developed group of polymers is the liquid-crystalline polymers showing orientational order but not positional order. They are thus intermediates between the amorphous and the crystalline polymers. The differences in crystallinity lead to differences in physical properties. [3]

1.1.4 POLYMER NAMES

One polymer can have several different names given to it. Each of the name categories describes some feature of the polymer.

Systematic name is that assigned according to nomenclature rules adopted by the International Union of Pure and Applied Chemistry. It completely specifies the chemical structure of the simplest mer of the polymer. The systematic name for PE is poly(methylene), that for polystyrene (PS) is poly(phenylethylene), and for PVC is poly(chloroethylene). Systematic names are not widely used, because the nomenclature rules are quite complicated. Many of the resulting names are quite lengthy, and other names have simply become accepted. [2]

Chemical name is used by polymer chemists in most of their descriptions. In some cases, this name is the same as the systematic name, and sometimes it is a shortened version of the systematic name, which groups together several slightly different polymers under one term. [2]

The chemical name is the most commonly used by polymer scientists. Therefore, we will generally refer to polymers by their chemical names in this work. These names are based on the names of the mer unit of the polymer or, for complex polymers, on the name of one or more prominent chemical groups that make up polymer. [2]

Customary name (or common name) often groups together even more polymers than does the chemical name. Such names are unpredictable; being derived from early marketing terms for the material, modified chemical names, or other sources. They are often used in a nonspecific sense to describe a group of polymers without using proprietary commercial names. Such names include vinyl, acrylic, and nylon. [2]

Commercial name is assigned by the company marketing the polymer and is usually proprietary. A given polymer may have several different commercial names, because several different companies may market the same polymer, and the same commercial name may refer to several different polymers. Some of these names, such as nylon, have been allowed to become generic and are now used as customary names. [2]

1.1.5 POLYMERIC MATERIALS

The properties of a polymer material are determined by the structure of the polymers used, the additives and the processing methods and conditions. It is possible to make an extremely stiff and strong fibrous material from polyethylene. Conventionally processed polyethylene has a stiffness of only about 1 GPa, whereas fibrous polyethylene may exhibit a longitudinal

modulus of 100 GPa. Some polymer materials are almost pure with only a small content of additives, whereas others consist of predominantly nonpolymeric constituents. Composites consist of reinforcing fibres and the function of the polymer is merely to provide the shape of the product and to transfer forces from one fibre to another. The reinforcing fibres give the material its high strength and stiffness.

Some polymer such as polyethylene may only contain a small portion of antioxidant to prevent the polymer from oxidizing. Other polymers, particularly for rubbers, contain both large numbers and large amounts of additives, antioxidants, an accelerator for vulcanization, and an inhibitor in order to avoid early cross-linking. An increasingly important field is the prevention of fire without the use of halogen-containing polymers. [2]

Thermoplastics and thermosets. One very important classification scheme is based on the response of the polymer to heat and solvents. There are two extreme types of response possible, leading to the classification of polymers as thermoplastics or thermosets. Polymers that reversibly soften and melt when heated or soften and dissolve when treated with an appropriate solvent are thermoplastics, while those that do not are thermosets. Thermoplastics are composed of linear or branched polymer molecules, and for that reason they melt. Thermoplastics are first synthesized and then at a later stage moulded. Thermosets are cross-linked polymers that do not melt. An uncrosslinked prepolymer is given the desired final shape and the polymer is cross-linked at a later stage while it is kept in the mould.

In the polymer molecule, formed from an order or statistical sequence of monomer units, "primary forces" hold the chain together. The degree of order, that is the special positions of the chains in the relation to each other, determines the "secondary forces" between the chains. These secondary forces are about one hundredth the strength of the primary forces. This difference in the bonding forces is characteristic of thermoplastics. They soften when heated, the chains sliding against one another. The plastic is reversibly moldable. Chain branchings or obstructing side chains increase the chain separation and lower the forces between them. A larger chain separation also raises the light transmittance. Irregular chain molecules with steric obstructions soften on application of heat and hardener in an entangled and disorderly manner. The solid is amorphous. If the chains have at least partial regions of order, the plastic is partially crystalline. Elastomers and thermosets are always amorphous. [4]

Because they can be softened, thermoplastics can be repeatedly reheated (or dissolved), and moulded, thermal – or solvent – welded, or shaped by multistep operations, unless there is some type of chemical degeneration or contamination. Examples of commodity uses for thermoplastics include polyethylene (PE) used in hot-melt glue guns or for plastic bags,

polyvinyl chloride (PVC) used to make plastic pipe and vinyl raingears, and polystyrene (PS) formed into disposable drinking glasses and a variety of children's toys. Examples of engineering plastics made from thermoplastics polymers are polyamide (PA), used, for example, to make unlubricated gears and ski boots; polycarbonate, used for compact discs and motorcycle helmets; and ultrahigh molecular weight polyethylene (UHMW PE), used to make ice hockey dasher boards and pen tips. Thermosets, on the other hand once reacted and cured, cannot be re-formed by any means that will not break the covalent bonds and destroy the polymer. Examples of thermosets include epoxy (EP), phenolic, and unsaturated polyester (UP) resins. Epoxies are used as both commodity and engineering adhesives and as matrices for high-performance composites. Phenolic resins are used in commodity applications such as ashtrays and cutlery handles, as well as for brake pistons and electrical connectors. Unsaturated polyesters are most often used in filled form, where they may be found in diverse applications ranging from cultured marble sink tops or helicopter rotor blades. [2]

Elastomer is a material that substantially recovers its original shape and size at room temperature after removal of a deforming force. [2] In addition to the usage of elastomers as such (rubber tubing, tyre tubes, etc.), dispersed elastomers are used to enhance mechanical properties of some brittle polymeric materials (e.g, in acrylonitrile-butadiene-styrene copolymers, ABS, or high-impact polystyrene, HIPS).

Thermoplastic elastomers. These materials are basically thermoplastics with the usual property that the moulding process is reversible. The cross-linking consists of blocks (sequences) of ordered copolymers, which are either partially crystalline or flexible. There are strong Van der Waals' forces between the closely packed partially crystalline segments, while the flexible segments show a certain degree of rubber elasticity. When heated, the partially crystalline and flexible regions soften and the copolymer can be plastically moulded. It sets on cooling reproducing the pseudo elastic behaviour. Another way to obtain thermoplastic elastomers is by mixing – in the partially crystalline matrix of a non-crosslinked rubber. These particles partially cross-link on heating and so are impact-absorbing. [4]

1.1.6 PROPERTIES OF POLYMERS

We cannot cover all polymer properties, but we will discuss the structural influences on some properties. The most important properties of polymers and the most significant influences of structures on those properties will be covered. [2]

Glass transition temperature is a typical feature for polymers. Next to the crystalline melting point temperature (T_m) of semicrystalline polymers, which is the characteristic of a

first-order thermodynamic transition, a second-order transition temperature – glass transition temperature (T_g) can be measured. It is defined as the temperature at which the coefficient of thermal expansion changes abruptly, i.e. at which the change in the slope of the temperature dependence of specific volume can be observed.

The value of T_g depends very substantially on the chemical structure of the macromolecular chain, namely on its mobility. The more rigid is the chain, the higher the T_g of the polymer. For crystallizable polymers, which exhibit both T_g and T_m, it holds that $T_g <$ T_m. An approximate empirical rule holds, $0.5 < T_g$ (K)/ T_m (K) < 0.8. The lowest glass transition temperatures reported are below $-100°C$. High-temperature imitations result from the fact that some polymers are destroyed at very high temperatures, earlier than their chains become mobile. Examples of T_g of some selected polymers are in the following table.

Table 1.1 Glass transition temperatures of selected polymers.

Polymer	T_g (°C)
Polystyrene (PS)	100
Polymethylmethacrylate (PMMA)	105
Polyvinylchloride (PVC)	81
Polybutadiene (PB)	- 60 to - 80
Polyethylene (PE)	- 125
Polypropylene (PP)	- 7
Polyamide 6 (PA6)	52
Poly(ethylene terephthalate) (PET)	67
Polytetrafluorethylene (Teflon, PTFE)	- 113

The approximate midpoint of the temperature range over which the glass transition takes place, glass fibres exhibit a phase change at approximately 955 °C, and carbon / graphite fibres exhibit the change at 2205 °C to 2760 °C. The temperature of which increased molecular mobility results in significant changes in the properties of cured resin system. Also in the inflection point on a plot of modulus versus temperature. The measured value of T_g depends considerably on the rate of temperature change in any experiment and on the frequency or rate of deformation in mechanical test. [2]

Molecules with well – defined geometric structures, such as sucrose (Common sugar), tend to crystallize when their solutions are cooled or concentrated by evaporation of the

solvent. Comparable crystalline structures exist in polymers with well-defined geometric structures such as linear polyethylene (PE), which is called high-density polyethylene (HDPE). Attaining regular arrangements of the long-chain molecules in the presence of other irregularly arranged chains is difficult. Therefore, these regularly shaped polymer molecules are usually not fully crystalline. The crystalline domains in a polymer such as HDPE are large enough to make the solid polymer opaque and to exhibit reproducible melting points, T_m, which are first-order transition temperatures. Glass and many polymers with irregular structures are non-crystalline, or amorphous. Unlike crystalline materials, they do not have exact melting points. They do change from brittle, glasslike materials into more flexible materials at reproducible, characteristic temperatures – glass transition temperatures, T_g, which are second-order transition temperatures. As crystalline polymers such as HDPE consist of crystalline and amorphous regions, both T_g and T_m characterize them: T_g is always lower than T_m. For example, the T_g for HDPE is - 90 °C, while its T_m is 135 °C. [2]

MECHANICAL PROPERTIES

Mechanical properties are the most important properties for construction applications. There are many mechanical tests adapted to individual polymeric materials and to specific shapes of products or construction parts.
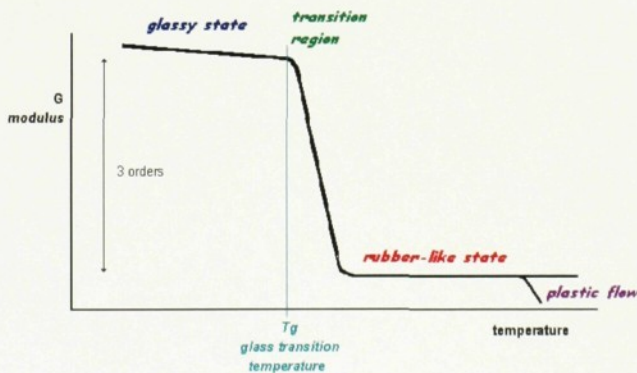

Fig. 1.3 Temperature dependence of polymer Young modulus.

It is not possible to cover the whole problematic and therefore only the most important features will be mentioned here. The basic mechanical feature of polymers is the specific dependence of their Young modulus on temperature (Fig. 1.3). At low temperatures, values of Young modulus are high while at high temperatures, well above the glass transition

temperature, the modulus drops by about 1000times. The high-modulus state is called the glassy state, the low-modulus one is the rubber-like state. The region in which the modulus drops substantially (the transition region) starts at the glass transition temperature. The extent of the rubber-like region depends on the molecular weight of the polymer in question. Thermoplastics exhibit plastic flow at high temperatures while thermosets, which can be considered as having infinite molecular weight, keep their modulus almost constant at high temperatures. [2, 3]

With the above-mentioned feature in mind, properties of a polymer at the room temperature differ substantially depending on its glass transition temperature. The polymers with T_g below the room temperature are rubber-like, those with T_g well above the room temperature are glassy and brittle.

Stress-strain curves are probably the most frequently used mechanical tests of polymers (construction plastics). They provide information about the character of the mechanical behaviour (brittle, plastic, rubber-like). Modulus (initial slope of the curve), parameters of the yield point, extensibility and strength, as well as work of deformation (area below the curve) can be measured. The curves can be measured at the room temperature or at elevated temperatures (with a heating chamber), and also with varying deformation rate. Polymers can be thus easily compared. [2, 3]
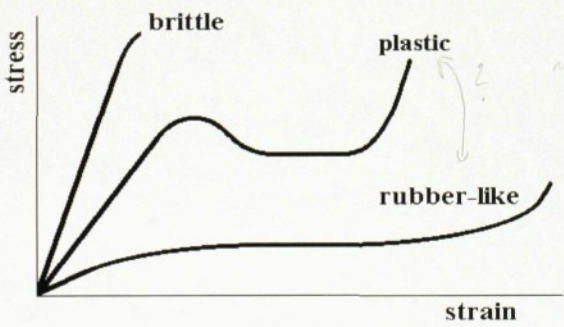

Fig. 1.4 Shapes of the stress-strain curves of various polymer types.

Depending on testing instruments, and parameters of testing and ambient environment, many other aspects of mechanical behaviour are measured, e.g. toughness, stiffness, (notch) impact strength. The particular application requires specific testing, results of which may be

more important than the others. They may be long-term tests, short-term tests, specific loading condition, influence of environment etc. [2, 3]

Stiffness is a factor involving shape of the testpiece in addition to the Young modulus of the material. Higher stiffness can be achieved by the higher material cross-section and by the higher modulus. The same factors that influence thermal expansion dictate the stiffness of a polymer. Thus in a thermoset, the degree of cross-linking and the overall flexibility of the units is most important. In thermoplastics, crystallinity and secondary bond strength control stiffness. [2]

Toughness is a parameter involving the work consumed by the material to be broken. It corresponds to the surface area below the stress-strain curve. For high toughness, a polymer needs both the ability to withstand load and the ability to elongate substantially without failure. It may appear that factors contributing to high stiffness will thus be required, but this is incorrect, because of the inverse relationship between flaw sensitivity and toughness. The higher the stiffness and yield strength of material, the more flaws sensitive it becomes. Because some load–bearing capacity is required to provide toughness, a trade-off of factors achieves high toughness. Because crystallinity increases both stiffness and yield strength, an increase in crystallinity usually decreased toughness. [2]

Strength. The concept of strength is much more complex than that of stiffness. Many different types of strength exist including short- and long-term strengths, static or dynamic strength, and impact strength. [2] Yield strength of a polymer is largely controlled by the bonding that holds the polymer together. In thermoplastics, both the intrachain covalent bonding and the interchain secondary bonding contribute to strength. [2] Rupture strengths in thermoplastics are increased much more readily by increased secondary bond strength and crystallinity than by increased intrachain covalent bond strength. [2]

THERMAL PROPERTIES

Include dimensional stability, thermal decomposition, thermal expansion, and thermal conductivity. [2]

Dimensional stability is the most important thermal property for majority of polymers, because a polymer cannot be used at a temperature above which it loses dimensional stability. For most polymers, the main determinant of dimensional stability is the glass transition temperature (T_g) of the polymer. Because of the partial or complete noncrystalline nature of polymers, they undergo a transition as a function of the temperature that is not seen in fully crystalline materials. This (T_g) is a measure of the temperature at which the noncrystalline

portions of the polymer change glass state at low temperature to a rubbery state at higher temperature. This is the most important temperature that can be specified for most polymers because in all but highly crystalline polymers it represents the temperature above which the polymer loses most of its stiffness and thus dimensional stability. [2]

Thermal decomposition. The thermal decomposition temperature of the polymer is largely determined by the elements and bonding within the mer unit. Thermal decomposition occurs when the primary covalent bonds of the polymers are ruptured. The decomposition temperature as well as the general chemical resistance of the polymer, is thus increased by stronger bonds, as well as by the inclusion in the mer of elements and bonds that are not easily attacked by chemicals or other agents. [2]

Thermal expansion. In a thermoset the ease or difficulty of thermal expansion is dictated for the most part by the degree of cross-linking as well as the overall stiffness of the units between links. Less flexible units are also more resistant to thermal expansion. Influences such as secondary bonding have much less effect on the thermal expansion of thermosets. [2]

In a thermoplastic, thermal expansion is controlled less by the stiffness of the chains than by strength of the secondary bonds between molecules. For example – thermoplastics held together by strong hydrogen bonds generally expand less than those held together by dispersion bonds. However thermal expansion is also generally reduced by crystallinity and the absence or presence of substantial crystallinity may greatly alter the thermal expansion of a polymer. [2]

Thermal conductivity also depends on primary and/or secondary bonding in that heat is conducted more easily thorough a polymer that is strongly bonded. Thus thermosets possess usually higher thermal conductivities than do thermoplastics. [2]

Crystalinity. In low-molecular crystalline substances, atoms or the whole molecules of a solid are regularly arrangement in space. In most polymers, this state is usually achieved only imperfectly. The crystalline regions are submicroscopic volumes in which there is some degree of regularity in the arrangement of the component molecules. [2] Quality and the quantity of the crystallised material depend on its thermal history. The portion of the polymeric material in regularly crystallographic arrangements is called crystallinity (in the percents of the total volume).

CHEMICAL PROPERTIES

Solubility of the polymer in various solvents and tendency for a solvent diffuse into and/or swell a given polymer are important considerations for many applications. The mutual

solubility of a polymer and a given solvent are strongly influenced by the elements and bonding within the mer and to a lesser extent, by the bonding between polymer molecules. This is because "like dissolves like ", which means that a polymer will not dissolve in a solvent unless the chemical structure of its mer unit is fairly similar to that of the solvent. [2]

Permeability. Secondary bonding is one of the most important influences on polymer permeability to gasses or other small molecules. If the molecule interacts strongly with a polymer, it will not be readily able to diffuse through it. Although this depends on a complex interaction between the polymer and the diffusant, an increase in the polarity of the polymer usually increases the interactions with the diffusant, thus reducing permeability. Usually strong polar or hydrogen bonding in polymer interferes with the permeability of polar molecules, while dispersive bonding has little influence. [2]

Chemical resistance. Although resistance to attack by chemicals, environments, and radiation depends on the chemical nature and bonding in the mer, it often depends even more on weak links in the polymer chain. Such weak links include chemical defects in the chain, branch points, and polymer end groups. Such weak links often have a much greater chemical effect than their concentration would indicate. The specialized chemical degradation problem knows as environmental stress cracking and crazing is produced by a combination of factors including solubility and polymer toughness. [2] Addition of antioxidants and/or stabilisers increases the stability of the polymer.

ELECTRICAL AND OPTICAL PROPERTIES

Dielectric and optical properties. Polymers are good insulators, they may be able to store electrical charge effectively, thus serving as good dielectrics. The dielectric constant of a polymer is improved significantly by the existence of permanent dipoles within the polymer. [2]

Conductivity. In most cases, polymers make poor electrical conductors. This is because the primary chemical bonding in most polymers is covalent, and thus there are no free electrons or ions to conduct charge. [2]

Dielectric strenght is greatly influenced by internal and external impurities. For example, PTFE has small permanent dipoles combined with a non-stick surface that does not gather surface impurities. It is viewed as an excellent dielectric material although its small dipoles do not store as much as bulkier dipoles, at least at low frequencies. As dielectric breakdown can also occur by mechanical or thermal collapse, dielectric strength is improved by increasing the basic mechanical strength of the polymer. [2]

Optical properties, such as colour, clarity, transparency, etc., may not seem to be very important properties, but if the polymer is to be used as a window in a jet aircraft, for example, such properties become very important. [2]

1.2 SILICONE POLYMERS

Silicones are synthetic polymers made from the products of nature. Although "silicone" is often used as a generic term for nearly all substances that contain a silicon atom, it is more properly described as an entirely synthetic polymer containing a Si-O backbone. To this backbone, organic groups are frequently attached to the silicon atoms via a Si-C bond.

This general description defines the broad class of polymers known as silicones. The most common example is poly(dimethylsiloxane) or PDMS. This polymer has a repeating $(CH3)2SiO$ unit. [5, 6, 7]

Fig. 1.5 Model of the PDMS chain. [7]
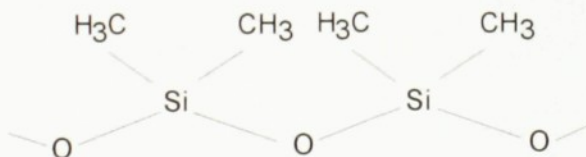
Fig.1.6 Part of the PDMS chain. [7]

These materials are the basic building blocks of the silicone industry. Depending upon the number of repeat units in the polymer chain and the degree of cross-linking ("tying" the

polymer chains together), at least six classes of commercially important products can be produced:

Emulsions, compounds, fluids, lubricants, resins, elastomers or rubbers. **[5, 24, 25, 26]**
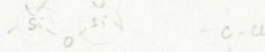
Silicones are made from silicon and methyl chloride in a process known as the "direct reaction" or "direct process." This reaction between silicon and our recycled reagents yields methyl chlorosilanes. They are distilled (purified), and the dimethyldichlorosilane is hydrolyzed to give PDMS. This product can be formulated or finished into thousands of different products, which are sold to every major industrial segment. **[5, 24, 25, 26]**

Silicones are highly valued materials because they have a combination of physical properties not found in other polymers. They have outstanding heat stability and can be used in applications where organic materials would melt or decompose. Many silicones seem to be impervious to the effects of ageing, weather, sunlight, moisture, heat, cold, and some chemical assaults. Some silicones are used to stick, bond, or couple things together – a glue. **[5, 24, 25, 26]**

Silicone rubber, a synthetic polymer, has a strong silicon - oxygen chemical structure that gives the elastomer its unique performance properties. Derived from quartz, rock, or sand, silicone rubber has an alternating silicon and oxygen backbone, unlike organic polymers made up of a less tenuous carbon-carbon band.
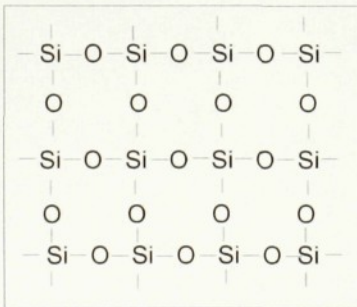

Fig.1.7 Model of silicone dioxide. **[11]**

The process of vulcanization transforms this structure, allowing the silicon-oxygen polymer to become an elastic rubber. [5, **24, 25, 26**]

Silicone rubbers can be sterilized, radiation and repeated steam autoclaving. **[6, 24, 25, 26]**

Silicones withstand a wider range of temperature extremes than nearly all other elastomers, remaining viable from −75 °C to 500 °C. [6, 24, 25, 26]

Silicone rubbers have high tear and tensile strength, good elongation, great flexibility and a hadness range of 5 to 80 Shore A. Softer durometers are available as reinforced gels. [6, 24, 25, 26]

Silicones exceed all comparable materials in their insulating properties as well as flexibility in electrical applications. They are non-conductive and maintain dielectric strength in temperature extremes far higher or lower than conventional materials can handle. [6, 24, 25, 26]

Silicones resist water and many chemicals, including some acids, oxidising chemicals, ammonia and isopropyl alcohol. However, silicones should not be used with concentrated acids, alkalines and solvents. [6, 24, 25, 26]

Silicones can comply with various norms for medical products. They are odourless and tasteless, do not support bacteria growth, and will not stain or corrode other materials. Most importantly, silicone rubbers exhibit superior compatibility with human tissue and body fluids. [6, 24, 25, 26]

1.3 FILLED AND REINFORCED POLYMERS
FILLED POLYMERS

Filler is a general term used to describe an organic, non-metallic or metallic powder added to resins. They can extend material for cost reduction and/or enhance the material's mechanical properties.

Fillers are used in polymers for a variety of reasons: cost reduction, improved processing, density control, optical effects, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy and improved mechanical properties, such as hardness and tear resistance. For example, in cable applications, fillers such as metakaolinite are used to provide better electrical stability while others, such as alumina trihydrate, are used as fire retardants. Each filler type has different properties and these in turn are influenced by the particle size, shape and surface chemistry. Filler characteristics are discussed from costs to particle morphology. Particle specific surface area and packing are important aspects. Filler loading is also critical and this is discussed. The terminology used in this field is explained and, where appropriate, illustrated. Practical aspects of filler grading are described. For example, the use of an average particle size on data sheets can be misleading as it may not accurately reflect particle size distribution. Different measuring conditions can also

give rise to variations in apparent particle size. The principal filler types are outlined. These include carbon black, natural mineral fillers and synthetic mineral fillers. The use of clay in nanocomposites is outlined. Carbon blacks are very important fillers, especially in the rubber industry. A brief description of their preparation and properties is not included. Filler surface modification is an important topic. Most particulate fillers are inorganic and polar, which can give rise to poor compatibility with hydrocarbon polymers and processing problems, among other effects. The main types of modifying agent and their uses are described, from fatty acids to functionalised polymers. Fillers are also discussed in relation to different polymer types. For example, in flexible PVC, because of the plasticiser, the filler has little effect on processing. This allows relatively high filler levels to be incorporated. This review is very clearly written by an outstanding expert in this field. Illustrations are included to explain concepts from microscopic filler structure to the effects of fillers on polymer properties. [23]

Characteristics of an ideal filler. Inert, constant properties, low specific gravity, ton-toxic, non-hazardous, non-abrasive, and low cost.

Chemical Properties Available. Most fillers used are inorganic and are usually based on naturally occurring mined minerals that are beneficiated in some cases. Some fillers are made synthetically, usually by precipitation from a solution of soluble salts.

Physical Properties Available. Particle size varies with the filler's specific grade, but can range from relatively coarse particles - a median particle size of 15 microns or more with 1 to 2 percent retained on a 45 micron screen. Some fillers are sized to very fine particles with a median particle size of well below 1 micron. The precipitated fillers usually have a finer and more narrow particle size distribution than the ground fillers.

Typical Applications. Widely used in coating powder formulations to modify functional properties, such as hardness, modulus, permeability, corrosion, abrasion, chip resistance, gloss, texture, flammability, and electrical characteristics. The physical properties of cured polysiloxane materials are dramatically influenced by fillers. So – called non – reinforcing (extenders) and reinforcing fillers are typically used; the most common reinforcing filler is silica. High surface area silica, called fumed silica. [2]

REINFORCED POLYMERS

Reinforced polymer is a term for polymer material with fibres like a filler. Carbon, glass and aramid fibres are now used extensively in polymer matrix composites. Fibres bring a typical properties, all have high stiffness and relatively low density. The most commonly used polymers are thermosetting resins like a epoxy resin, unsaturated polyester, vinyl ester. These

cover a very broad class of chemicals and a wide range of physical and mechanical properties can be obtained.

One of most significant features of thermoplastics composites is that processing tends to be more difficult than thermosets. This is essentially because they are already polymeric, and hence highly viscous even when liquid, before the composite is fabricated. There are for examples polysulphones, polysulphides, polyimides. The fibres are particularly short. [2, 23]

1.4 INTERFACES

Composite materials consisting of more than one distinct phase are in general use in modern industrial application. There are a lot of suitable matrices for this class of material. The reinforcement phase has advantage of strengthening the composite, enabling, by proper design, to reinforce the matrix in the required amount. The reinforcing phase should have a high melting point, low specific gravity, high strength over the whole range of working temperatures, minimum solubility in the matrix, high chemical stability, absence of phase transformations over entire temperature range, and non-toxicity during production and servicing.

The role of matrix is to protect the filler from corrosive action of the environment and to ensure interaction between the filler unit by mechanical and other effects. However, around inclusions embedded in a matrix a rather situation develops, with areas of imperfect bonding, mechanical stresses due the shrinkage, high stress gradient or even stress singularities due to the geometry of the inclusion, voids, microcracks, etc. The interactions of the surface of the filler with matrix are usually more complicated and not simply of mechanical nature. The filler actually restrict the segmental and molecular mobility of the polymeric matrix, as adsorption-interaction in polymer surface-layers occurs with particles. Under these conditions the quality of adhesion can hardly be quantified making investigations necessary.

The boundary layer between phases, lying near the interface, plays the role of a barrier to crack propagation, of a wave- and energy-reflector for the stress waves accompanying the propagating cracks, of an attenuator of the fracture phenomenon, and a damped of crack propagation. Although the strength of a composite is mainly depending on the properties of its consisting phases, there is another major parameter determining the properties of a composite system. This parameter depends on the effectiveness of bonding between phases in transferring stresses across the interfaces of two the main phases.

Introducing filler into a polymeric matrix results in the production of a composite material with superior strength. However, predicting the properties of the product is difficult, since they depend on a great number of parameters. Attempts to predict such features may only lead to a rough estimation of the influence of fillers on the overall behaviour of the composites. For example, a linear increase of the strength of the composite is observed as a filler-volume fraction increase. However, the reinforcing action of the filler is limited by the nature, shape and grade of the filler, and, on the other hand, by adhesion efficiency between the two phases and the mechanism of failure of the composite system. Also, another important factor affecting the strength properties is the interaction between individual filler particles. This last parameter is difficult to predict in a real composite. [8, 27]

2 EXPERIMENTAL

2.1 MATERIALS

2.1.1 FILLERS

Filler is a general term used to describe an organic, non-metallic, or metallic powder added to polymers. Fillers can extend material for cost reduction and or enhance the material's mechanical properties.

Table 2.1 Types of fillers used in experiments.

Designation Of Fillers	Commercial Mark	Content of SiO$_2$ [%]	Content of Water [%]	Specific Gravity [g/cm^3]	pH	Medium Average of Particles [μm]	Surface Area [m^2/g]	Shape of Particles
Silicon Dioxide fumed	CAB-O-SIL (type M-5)	99.8	1.5	2.2	3.8 – 4.2	Primary 10 – 30 nm Aggregate 0.2 – 0.3	200±15	Spherical
Silicon Dioxide Precipitated	Siloxid	98.0	8 - 12	2.05	6.5 – 7.4	20	80	Spherical
Quartz Sand		99.3 – 99.7		2.65	7.5	100 - 60		Grains
Siliceous Microlamella	Glass Flakes	60	5 – 6.5	1.8 – 1.9	12	Length 20		Lamellar
Nanoclay Montmorillonite	Cloisite Na$^+$	50	2	2.8		6		Lamellar
Glass Bubless	Scotchlite S 60	60 - 80	-	0.60		30	0.9 -2.7	Spherical

SILICON DIOXIDE - FUMED – CAB-O-SIL – TYPE M-5

Cab-O-Sil fumed silica is produced by vapour phase hydrolysis of silicon tetrachloride in a hydrogen oxygen flame. The reactions are:

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

$$2H_2 + O_2 + SiCl_4 \rightarrow SiO_2 + 4HCl$$
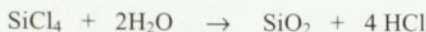
The combustion process creates silicone dioxide molecules, which condense to form particles. The particles collide, attach, and sinter together. These processes result in three – dimensional branched chain aggregate with a length of approximately 0.2 – 0.3 microns. Once the aggregates are cooled below the fusion point of silica (1710 °C), further collisions results in mechanical entanglement of the chains, agglomeration. Further agglomeration takes place in the collection system to yield a fine white fluffy powder with an agglomerate size less than 44 microns.

The most important and widespread use of fumed silica in liquid system is for the control and increase of viscosity and thixotropy. Fumed silica has the ability to reinforce or increase the cohesive strength of a solid system. The reinforcing effects produced by fumed silica are similar to those carbon black and it has been called the "white carbon black". [9]
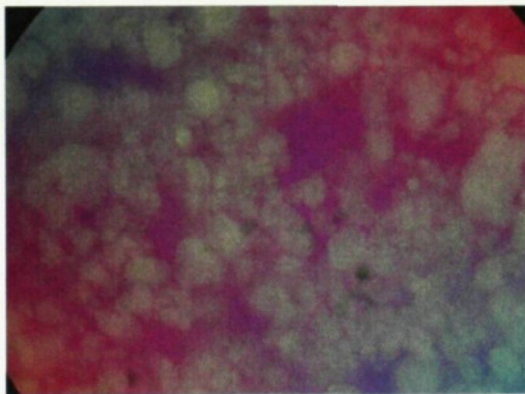
Fig. 2.1 Micrograph of fumed silicon dioxide
(light microscopy, frame width 1500 μm).

SILICON DIOXIDE – PRECIPITATED – TYPE SILOXID

Precipitated amorphous silicon dioxide has a form of soft powder, with small-size particles, which are developed by chemical reaction between sodium silicate and hydrochloric acid in water environment by equation:

$$Na_4 SiO_4 + 4 HCl + water \rightarrow 4 NaCl + 2 H_2O + SiO_2 . water$$

It is important to remove sodium chloride by decantation, from precipitated amorphous silicone dioxide, eliminate surplus water, and dry up the sample. Average specific surface of the precipitated SiO_2 is 80 m^2/g. This type of silicon dioxide, also called white smoke particles, is used for filling thermoplastics, resins, and elastomers. Precipitated amorphous silicone dioxide is similar with some properties with an amorphous fumed silicone dioxide. [10, 11]
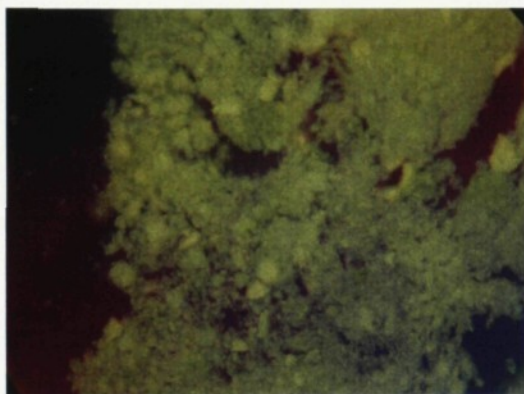
Fig.2.2 Micrograph of precipitated silicon dioxide
(light microscopy, frame width 1500 μm).

QUARTZ SAND

The sand used as the filler originates from the Czech locality Střeleč. After mining, the raw material is processed by filtering, flotation, milling, and separation. It is used mostly as inexpensive filler to polymeric systems, mainly reacto-plastics.
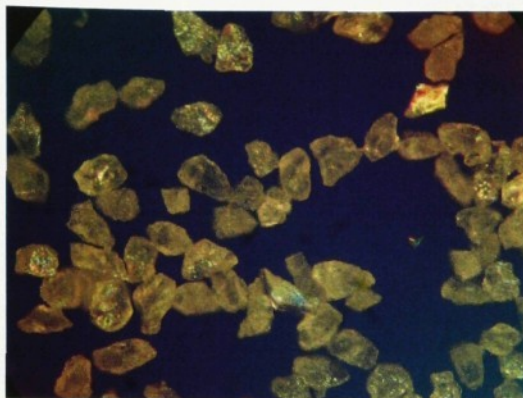
Fig. 2.3 Micrograph of quartz sand
(light microscopy, frame width 1500 µm).

GLASS FLAKES¤

Glass flakes is a glass powder, particles of which are irregular non-crystalline glass platelets, shape of which is irregular. Mean particle size as given by its producer is 16 µm, density 1800 – 1900 kg/m^2, maximum content of SiO_2 60 wt.%. It can be considered as a pigment with barrier properties (hindering penetration and transport of liquids and gasses through the polymer matrix containing it), which increases resistance of the system against water diffusion, corrosive gasses and salt solutions. The platelet structure also supports high resistance against mechanical loading of paints containing the filler. Thanks to low density, the tendency to the particle sedimentation is low. [12]

Glass flakes are manufactured by milling of hollow glass bubbles. Polymers with this filler used as reinforcement for thermoplastics because the filler gives the material high weld strength and impact strength, and improves dimensional stability. Therefore, they have numerous applications in various industries: in chemical plants, marine construction and harbour facilities, petroleum tanks, pollution control facilities, metal plating industries, boiler and water tanks, food industries, transportation concerns, fishery concerns, and livestock concerns. [13, 14]
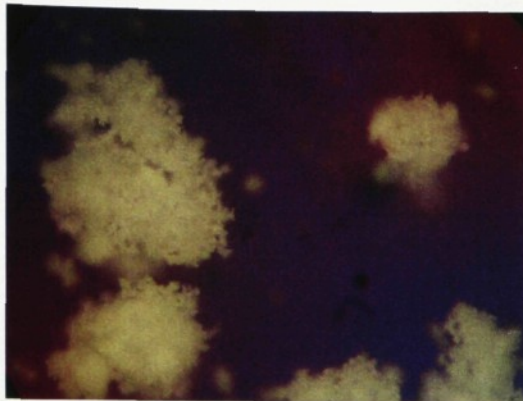
Fig.2.4 Micrograph of glass flakes

(light microscopy, frame width 1500 μm)

MONTMORILLONITE [K+0.58(Al,Mg)2(Si,Al)4O10(OH)2] - NANOCLAY

The montmorillonite group of minerals are clay minerals formed from very small and imperfect crystals. This group is basically of the pyrophyllite-type but substitutions in either or both octahedral and tetrahedral layers allows weak bonding of exchangeable cations in interlayer positions. Interlayer water or cation exchange occurs readily, with accompanying large changes in the c-dimension, hence the term 'swelling clays'. The simplest end-member formula (which is that of pyrophyllite) is $Al_4Si_8O_{20}(OH)_4.nH_2O$; the term 'smectite' encompasses the group of clay minerals that are derived from this formula.

Nanoclays are produced by Southern Clay Products, Inc., of Texas, USA. They are high aspect ratio additives based on montmorillonite clay. In this study, we used Cloisite Na+ T 42, a product of the above company.

When dispersed in both thermoplastic and thermosetting resins, montmorillonite (cloisite) nanoclays can give the following performance advantages to the finished product: Increased modulus and tensile strength, increased barrier properties to moisture, solvents, chemical vapours, gases and flavours, reduced UV transmission, increased dimensional stability, higher heat distortion temperature, good recycling properties, flame-retardant properties. The plastic will dye more easily, the appearance of painted parts is improved, and static cling in films is reduced. [15]
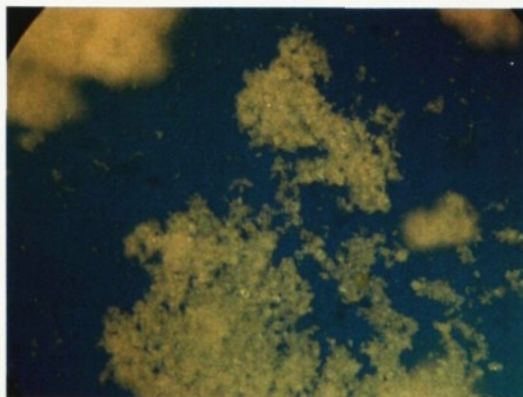
Fig. 2.5 Micrograph of montmorillonite
(light microscopy, frame width 1500 μm).

3M GLASS BUBBLES – SCOTCHLITE S 60

Glass bubbles are manufactured in a multi-step process in which glass is formed at high temperature from soda-lime-borosilicate, milled to fine particle size, and then run through a high-temperature heat transfer process.

Glass bubbles are hollow glass microspheres that can be added to epoxies and polyesters to fill surface imperfections and allow for easy sanding. Glass bubbles serve a variety of markets and applications, ranging from low-density void fillers for the aerospace market to antichip coatings, rocker panels, and bumpers for the automotive industry. Glass bubbles are used to produce syntactic foam for buoyancy and insulation in the oil and gas industry, and incorporated with polyester resins to produce artificial marble for fireplaces and baths.

Glass bubbles are valued for their extreme strength, low density, and chemical inertness. They can be cost effective weight reducers in sealers, adhesives and molded plastic parts. [16]
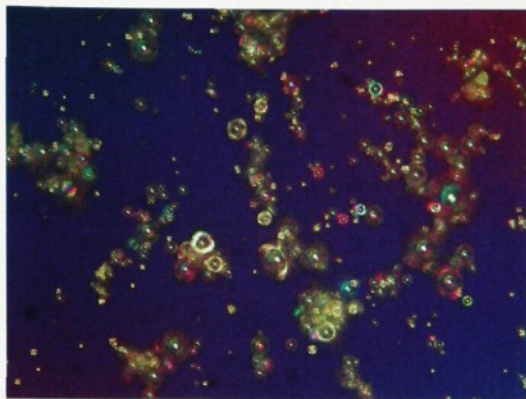
Fig. 2.6 Micrograph of glass bubbles
(light microscopy, frame width 1500 μm).

2.1.2 POLYMER MATRIX

LUKOPREN N 1000 (PDMS) was used as polymer matrix. This material has not carbon – carbon bonds and it is made only from siloxane chains with methyl groups, which are connected on silicon atoms. Lukopren N 1000 is chemically α,ω – dihydrodimethylsiloxan and belongs among two-component condensation type of silicone rubber. Details of the chemical processes are given elsewhere. [17] After mixing a viscous liquid with the crosslinking agent and catalyst, during a few minutes, all mass is going to be crosslinked and the silicon rubber is created. 8 volume percent of catalyst C 21 used for crosslinking of silicon rubber was added. We can see the crosslinking reaction on the following figure:

$$
\begin{array}{ccccc}
\text{R} & & & & \text{R} \\
| & & & & | \\
-O-\text{Si}-\text{OH} & C_2H_5O & O\,C_2H_5 & \text{HO}-\text{Si}-O- \\
| & & & & | \\
\text{R} & & & & \text{R} \\
& + & \text{Si} & + & \rightarrow \\
\text{R} & & & & \text{R} \\
| & & & & | \\
-O-\text{Si}-\text{OH} & C_2H_5O & O\,C_2H_5 & \text{HO}-\text{Si}-O- \\
| & & & & | \\
\text{R} & & & & \text{R}
\end{array}
$$

$$- O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O \qquad O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O -$$

$$Si \qquad\qquad + \quad 4 \; C_2H_5OH$$

$$- O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O \qquad O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O -$$
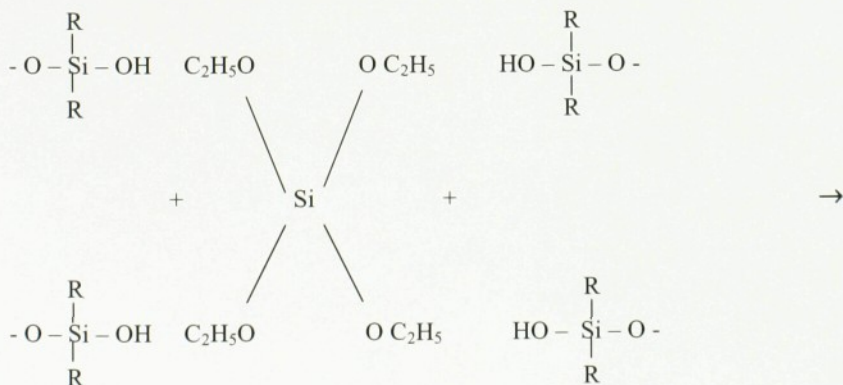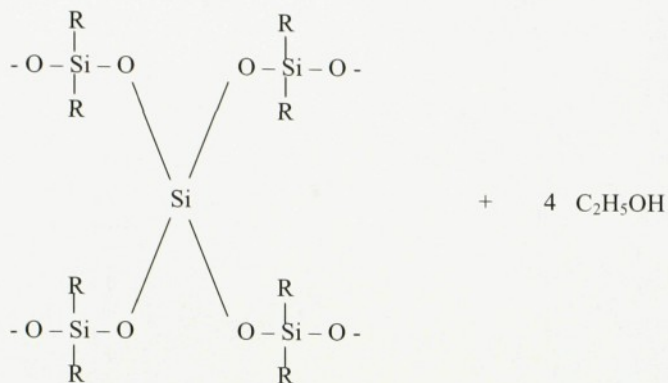
Fig. 2.7 Chemical reaction of silicone monomer with crosslinking agent.

2.1.3 CROSSLINKING AGENT

C 21 (mixture of crosslinking agent – dekaethoxytetrasiloxan and dibutyltin dilaurate) in concentration of 8 volume percent was used as crosslinking agent. [18]

2.1.4 SEPARATOR

To separate easily the silicone samples from moulds, separator based on polyvinyl alcohol delivered by producer was used. Thin separator film was formed on the mould surface, chemically inert to the crosslinked polymer, providing the separation. [18]

2.2 SPECIMEN PREPARATION

Samples were prepared by mixing of selected quantities of the silicone polymer, filler, and catalyser. Special detachable (demountable) moulds that are advantageous for the casting technology were used. Sample cross-section (32.0 ± 0.6) mm^2 was optimized with respect to the material used, and the possibility of crosslinking in the higher-pressure vessel. Length of the samples was (70.0 ± 0.1) mm.

Air bubbles put in the polymeric system as the result of stirring caused rather high inhomogeneity of the measured samples. Therefore, they were polymerized at the enhanced pressure about 0.8 MPa for 24 hours. The pressure vessel with the equilizing vessel were connected to a compressor providing the high pressure.

To prevent from sedimentation of the heavier filler particles, the chemical reaction was accelerated. To that reason, 0.8 vol. % crosslinking agent C21 was used.
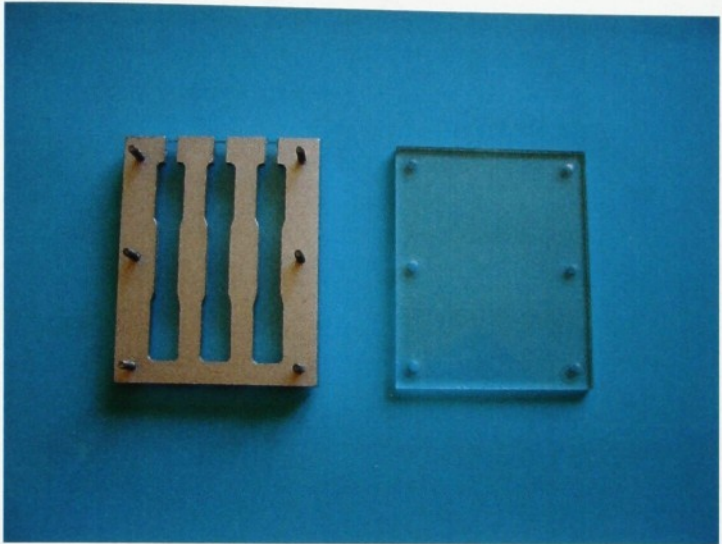
Fig. 2.8 Photograph of the used mould.
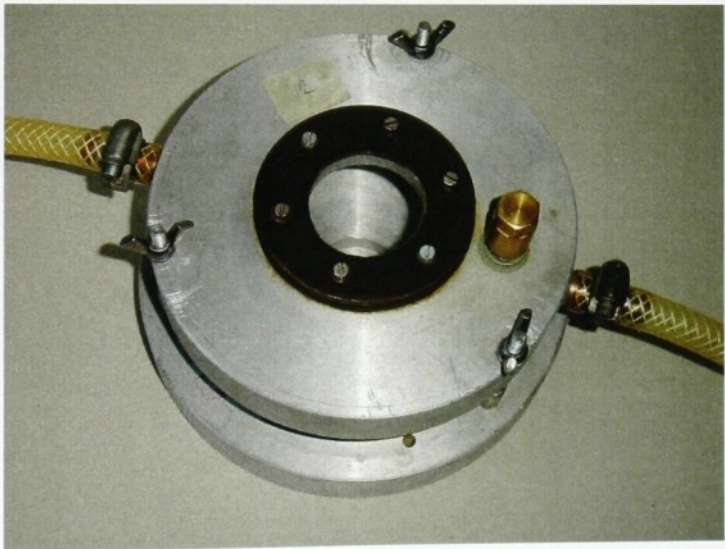
Fig. 2.9 Photograph of the pressure vessel.

2.3 EVALUATION METHODS

2.3.1 STRESS–STRAIN METHOD

The stress-strain test in tension is the most frequent and the most important measurement of mechanical properties of materials, not only for polymers. It serves to evaluate material behaviour by action of the tensile force with constant elongation rate. The tested specimen is deformed until it breaks, and both the acting force and the resulting elongation are recorded. Stress-strain dependence is recalculated.

The test piece, which has a simple shape (circular or four – square profile) is fastened into clamps of the tester and it is stretched with a selected clamp speed until the integrity of the test piece is disturbed. Axial tensile force F depending on the elongation of sample is recorded. This test monitors the most important mechanical properties. It is a short-time test; the sample is damaged within a minute, depending on the clamp speed and maximum elongation reached. Tensile strength R_m is obtained as the maximum value of the ratio of the force divided by the cross section S_0 of the sample. We can calculate the tensile strength by the formula:

$$R_m = F_m / S_0 \ [MPa],$$

where F_m - is the maximum force, and

S_0 - is the original sample profile.

Deformation A can be expressed as

$$A = (L - L_0) / L_0,$$

$$\Delta L = L - L_0,$$

where   L – is the measured length of the loaded sample, and

L_0 – is the original length of the sample.

For the stress-strain tests, dimensions of the test piece are measured in mm, and are put in the memory of the tester computer, and the computer does all the necessary recalculations.

During testing, cross-section of the measured sample decreases. Measurement of the actual cross-section is very difficult, therefore it is usually not performed, and all the values of stress R are related to the original cross-section.

Dimensions of the samples were measured with a slide rule. Stress-strain measurements were obtained with INSTRON 4204 (Instron Corporation, U.S.A) at the room temperature and relative humidity 50 %. Cross-head speed was 50 mm/min. **[19]**

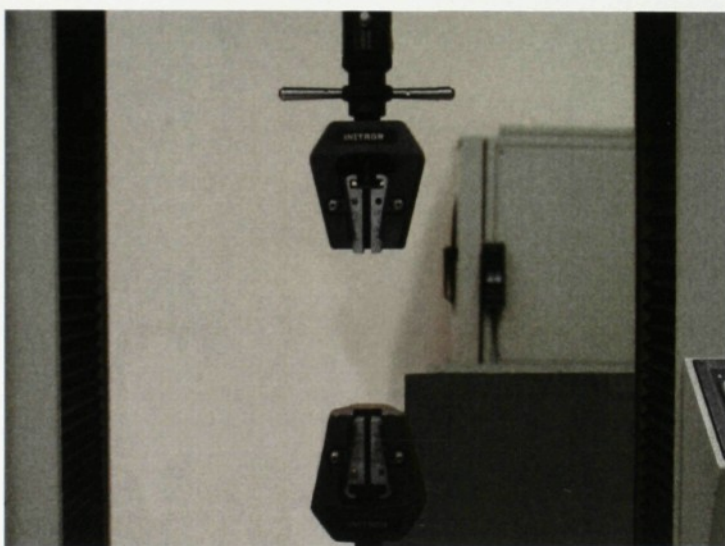Fig. 2.10 Tensile tester used for measurements.

Fig. 2.11 Clamps of the tensile tester used.

2.3.2 MICROSCOPY

Visible light transmission microscopy was used to visualize the original fillers (Figs. 2.1 – 2.6). Filler powder was spread on the microscopy slide and observed with model EPIPHOT microscope (Nikon) using the Nomarski method. Stereomicroscopy in reflected light

(Stereomicroscope Zeiss SMX20) was used to qualitative characterization of the filler dispersion in the matrix.

Sample preparation technique that we used to visualize fracture surfaces of the studied systems with scanning electron microscope is called soft matrix fracture surface technique (SMFS). [20] Fracturing in the state when the matrix is soft (rubbery), hard particles dispersed in the matrix can be clearly seen if the interfacial adhesion is low.

Microscopy preparation procedure:

1. Sample was provided with a small notch. Razor blade was used to make a cut about 1 mm deep in the smaller side of the sample cross-section, perpendicular to the longer dimension of the sample.

2. Slow tension in hands causes breaking the sample. Fracture thus obtained starts in the notch. Each of the two fracture surfaces obtained can be used for observation.

3. Specimen was trimmed to adjust its size to observation: The sample was cut with a razor blade in the distance about 3 mm from the fracture surface, and the cut surface was fastened to a substrate (a metal cylinder about 5 mm in height and about 10 mm in diameter).

4. The specimen (sample fastened on the substrate) was surface-coated with a thin layer of platinum (thickness about 4 nm). For surface coating, vacuum sputtering device SC 50 (BALTECH) was used. The metal surface coating has two main functions: First, to increase the signal (increase in the amount of the secondary electrons, which are detected. Second, to provide grounding of the sample, this leads away the accumulated electrons from the specimen and thus prevents the sample from charging.

To obtain scanning microscopical image, scanning electron microscope Vega TS 35 (Tescan Brno, Czech Republic), was used. Digital images were recorded. [20]

2.3.3 SWELLING

The specimens were swollen in chlorbenzene in time steps, and changes of the volume were observed from the sample dimensions. As the sample was proved to be isotropic, measurement of one dimension is sufficient.

3 RESULTS AND DISCUSSION

3.1 MECHANICAL MEASUREMENTS

An example of the results directly obtained from the stress-strain tester is in Fig. 3.1. The result is the dependence of load on the displacement for the silicone rubber Lukopren N 1000 with 6 phr of precipitated silicon dioxide Siloxid. All the results discussed further were obtained from similar graphs after recalculation, which is performed directly by the tester computer. Six test pieces were measured for each sample. Mechanical parameters of measured systems are in Figs 3.2 – 3.4.
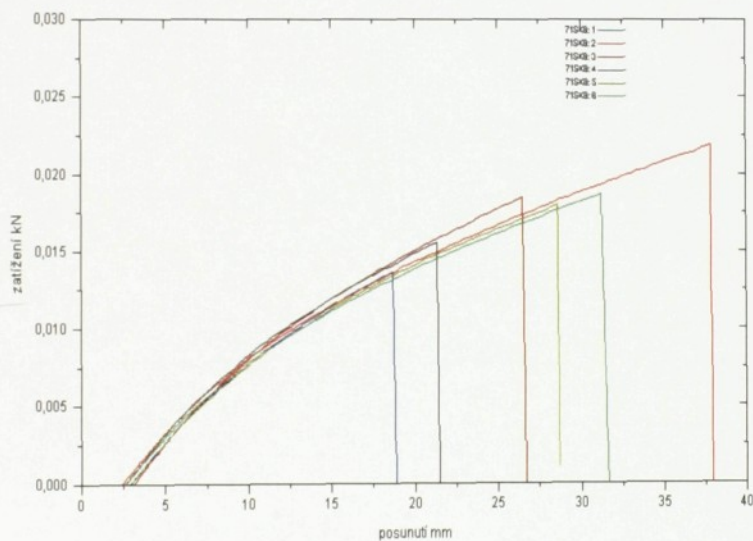
Fig. 3.1 Example of the measured dependence of load on the displacement for the silicone rubber Lukopren N1000 with 6 phr of precipitated silicon dioxide Siloxid.
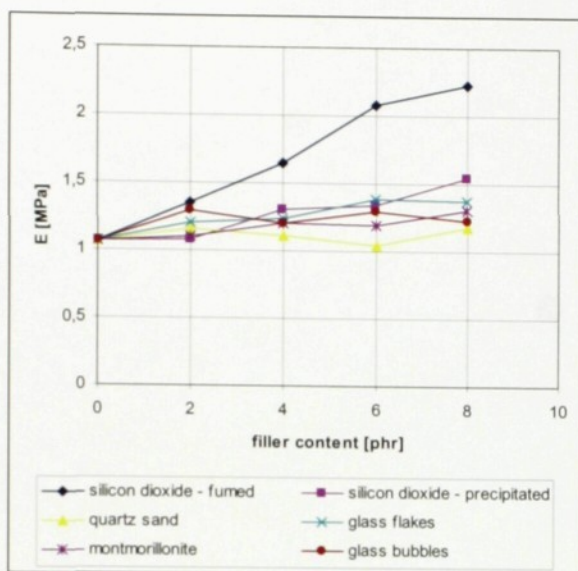
Fig. 3.2 Dependence of Young modulus of the silicone rubber on the degree of its filling with selected fillers. Phr is weight amount of filler per hundred weight parts of rubber.
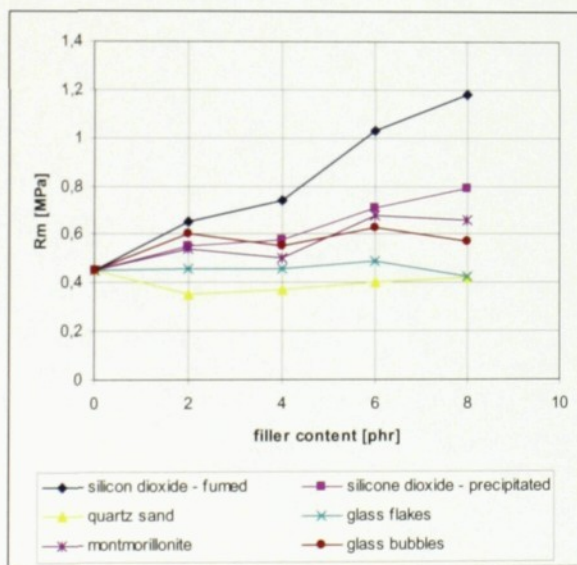
Fig. 3.3 Dependence of tensile strength R_m of the silicone rubber on the degree of its filling with selected fillers. Phr is weight amount of filler per hundred weight parts of rubber.
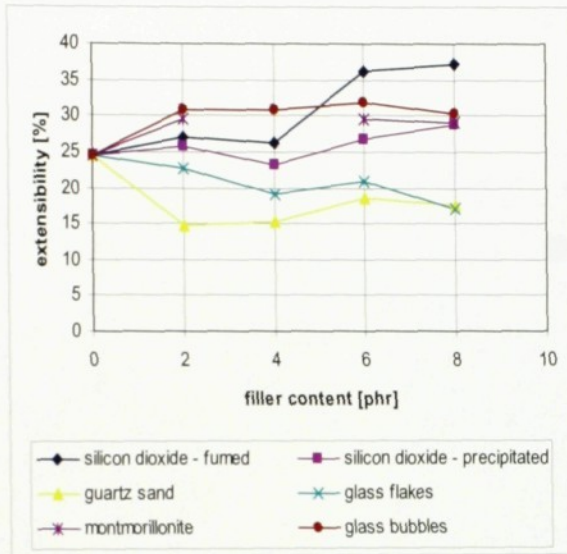
Fig. 3.4 Dependence of extensibility (ultimate deformation) of the silicone rubber on the degree of its filling with selected fillers. Phr is weight amount of filler per hundred weight parts of rubber.

There are several problems that we meet to perform the tests of the soft specimens:

- Measurement of dimensions of the sample (thickness and width). Care must be taken using common tools (slide calliper rule) as the force applied to the tool deforms the sample. This fact leads to systematic measuring errors, namely shortening the dimensions.
- The force needed to fasten the soft samples in clamps:
    1. If it is too high, additional stresses lead to fracturing the sample outside the gauge lengths of the sample, the length of which is measured and stored in the computer memory (frequently fracture in clamps).
    2. If the force is not high enough, the specimen will slide in clamps giving wrong measured values.

3.2 MICROSCOPY

Optical microscopy, transmission electron microscopy and scanning electron microscopy are major techniques for the assessment of morphology of semicrystalline polymers, liquid-crystalline polymers, polymers blends, and polymer composites including filled polymers. The list of applications in other areas of polymer science and technology is extensive.

Optical microscopy can resolve objects in specimen as small as 1 μm. Depth of field is relatively narrow, making the assessment of topographical features difficult in many cases, particularly when rough fracture surfaces are studied. Sample preparation is generally simple. Variations in absorption coefficient, sample thickness, refractive index and birefringence can be converted to contrast (light intensity) with the available optical microscopy techniques in the final image. Polarized microscopy, phase-contrast microscopy and differential interference-contrast microscopy convert differences in optical path (sample thickness, refractive index and birefringence) to variations in light intensity. Assessment of superstructure (spherulites, axialites, etc.) of semicrystalline polymers and mesomorphic structure (nematic, smectic, etc.) of liquid-crystalline polymers are important applications of optical microscopy.

Scanning electron microscopy produces detailed topographical images. The image is obtained by recording the scattered secondary electrons. The resolution limit is typically between 10 to 30 nm. The depth of field is very large and sharp images can be obtained for specimens with large topographical variation. Sample preparation is relatively simple. Information about morphology is obtained from a topographical analysis of fracture surfaces and etched specimens. All polymeric samples have to be coated with a thin layer of conductive material prior to examination by SEM. Some scanning electron microscopes are equipped with an X-ray microanalyser and these instruments can detect additives and "foreign" particles containing heavier elements.

Transmission electron microscopy produces detailed images of the density variation in bulk samples and topographical variations. The resolution limit is below 1 nm and depth of field is large. Sample preparation is difficult. The naturally occurring density variation in polymers is generally small and in order to achieve contrast, it is necessary to add heavier elements selectively to one of the phases. This procedure is referred to as staining. Osmium tetraoxide, reacting with unsaturated polymers, and chlorosulphonic acid, reacting selectively with amorphous component of polyethylene, are two important staining agent. Another type of preparation technique for specimens for TEM is etching, which may further be divided into solvent etching and chemical etching. Permanganic acid is the most useful etchant for a great

variety of semicrystalline polymers. The replica technique is possible to assess the topography of the etched samples. [3]

Transmission electron microscopy is not applicable for our systems because of principal difficulty in particle preparation. Sectioning ultrathin sections with an ultramicrotome would be possible only in the case of the matrix. However, presence of inorganic hard particles in it makes ultrathin sectioning impossible. The only applicable microscopy technique for obtaining information on the inorganic filler/polymer matrix system is scanning electron microscopy of fracture surfaces.

In this study, we have an amorphous polymeric matrix, transparent with no light absorption and with no detectable supermolecular structure. Therefore, we cannot expect any new facts on the matrix structure revealed by visible light microscopy. On the other hand, the fillers used have particle sizes that can be easily observed with light microscopy. Together with the transparency of the silicone matrix, distribution of the particles in the matrix can be observed a low magnification. Stereomicroscope, which has relatively high depth of field at low magnifications, can tell us whether the particle distribution is uniform through the sample or if a sedimentation of heavier filler particles occurred during the sample preparation. Those facts then can help at the interpretation of the results of mechanical measurements. Another possibility to use visible light microscopy in our study is to characterize fillers.

Optical microscopy technique was used to characterise differences between the individual filler morphology (Figs. 2.1 – 2.6). It is impossible to distinguish the individual particles, which are smaller than the resolution limit of the technique. The practical resolution depends also on the way in which the specimen is prepared. In our case, it was difficult to disperse the aggregates that are usually powdery materials. Therefore, in the image of fumed silicon dioxide, only the aggregates could be observed (Fig 2.1). In precipitated silicon dioxide, aggregates of small particles could be observed (Fig. 2.2); individual particles could be observed as well. Individual particles of the quartz sand were easy to observe (Fig. 2.3). In the specimen of glass flakes, small particles in the aggregates could be distinguished (Fig. 2.4). Similarly, the same holds for montmorillonite (Fig. 2.5). Mainly spherical particles and rather small aggregates were observed in the filler designated as glass bubbles (Fig. 2.6).

Sedimentation and aggregation was evaluated using a stereomicroscope. Results are in Table 3.1. Particle size, aggregation, and sedimentation are important data as they can help to explain mechanical behaviour of the systems.

Table 3.1 Qualitative evaluation of filler aggregation and sedimentation in the silicone rubber matrix.

Filler	Particle size from Table 2.1	Aggregation	Sedimentation
Silicon dioxide fumed	20 nm	No	No
Silicon dioxide precipitated	20 µm	Few big	No
Quartz Sand	100 – 60 µm	No	Very slight
Glass flakes	length 20 µm	Many big	Aggregates yes
Nanoclay Montmorillonite	6 µm	Small	No
Glass Bubless	30 µm	No	No

Fracture surface of the neat silicone rubber sample (without any filler) is characteristic by its fracture textures, which start to be created from a notch (Fig. 3.5a, left side). Because of the complicated stress concentrations in the vicinity of the notch as well as around the spreading crack, the fracture textures may have very different shapes (Fig. 3.5). When inspecting fracture surfaces, we observe their borders, which are seen as fracture curves. These can have very different geometrical shapes [21]; one example is on (Fig. 3.5c). If no filler is present, nothing more can be seen from the fracture surface: between the fracture curves is the fracture surface otherwise smooth even at high magnifications (Figs 3.5b, c).

Another phase present in the system influences mechanical behaviour of the whole systems. Differences in the mechanical properties of the individual components influence spreading of the fracture front and mark the fracture surface. Consequently, particles dispersed in a matrix can be found on a fracture surface.

SEM MAG: 178 x   DET: SE Detector
HV: 30.0 kV   DATE: 04/27/04   500 µm   Vega ©Tescan
VAC: HiVac   Digital Microscopy Imaging

Fig. 3.5a [6757]
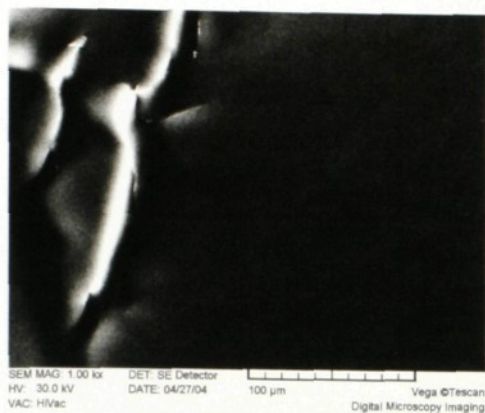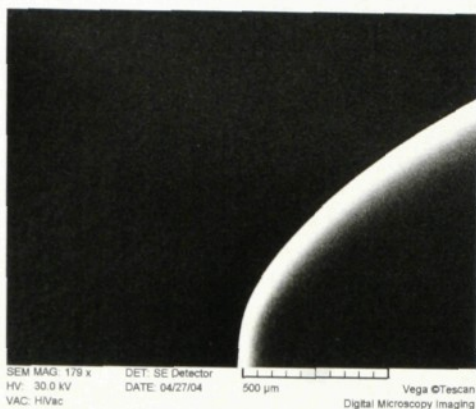
Fig. 3.5b [6756]   Fig. 3.5c [6758]

Fig 3.5 Fracture surfaces of neat silicone rubber. SEM.

This is particularly distinctive when interfacial adhesion between the components is low [20]. In our filled samples we could find that filler particles can be observed that way and that the are differences between the systems studied.

In some samples, sedimentation effect was be observed. If the filler particles are big enough, during the polymerisation of silicone the more dense particles tend to move to the bottom of the mould. In spite of that the polymerisation was accelerated, the sedimentation effect happened.

Silicone rubber filled with quartz sand is the only sample where the sedimentation effect was observed from fracture surfaces. Sedimentation can be observed even at low magnifications in images of the same fracture surface taken from the regions close to the opposite surfaces (Fig. 3.6a, b, sample with 8 phr). Filler particles are seen very clearly on the fracture surface, which means that the interfacial adhesion is low. Despite the chemical similarity of the filler to the matrix, big particle size has a predominating effect.
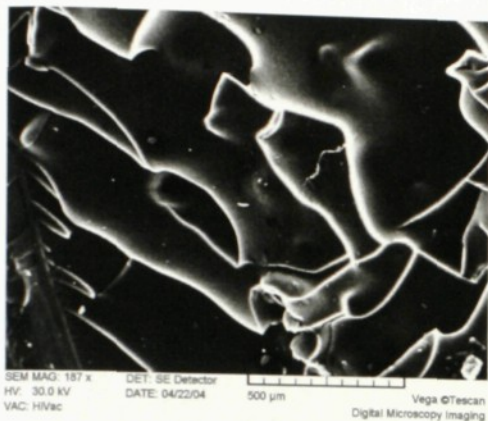
Fig. 3.6a [6706]

Fig. 3.6b [6704]
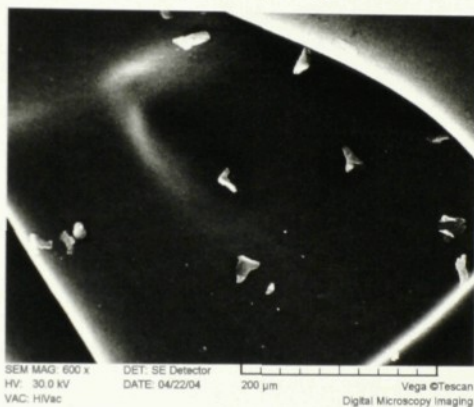
Fig. 3.6c [6703]

Fig 3.6 Fracture surface of silicone rubber with 8 phr of quartz sand. Place close to upper surface (a), and a place close to lower surface of the sample (b,c). A part of notch is seen left in (b). SEM.

Another effect was observed taking place in our samples, namely filler aggregation (see also Table 3.1). Silicone rubber filled with glass flakes can be an example (Fig. 3.7). Next to the dispersion of the filler particles in the matrix (no pronounced sedimentation is observed, c.f. Figs 3.7a, 3.7b), big aggregates of the filler are observed (Figs 3.7b, 3.7d). Cavities in the aggregates (Fig. 3.7d) give evidence that silicone matrix does not penetrate into the aggregates completely. Negative influence of the aggregation on mechanical properties can be expected.

Fig. 3.7a [6708]
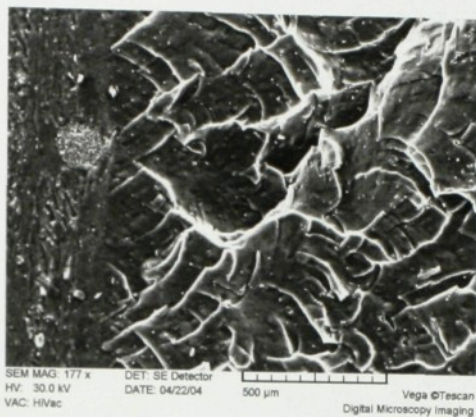
Fig. 3.7b [6710]
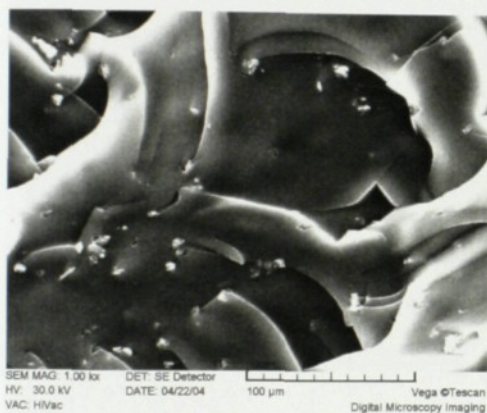
Fig. 3.7c [6707]
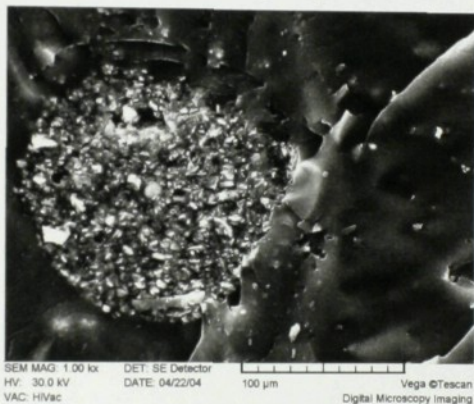
Fig. 3.7d [6711]

Fig. 3.7 Fracture surface of silicone rubber with 8 phr of glass flakes. Place close to one surface (a, c), and a place close to the other surface of the sample (b,d). A part of notch is seen left in (b). SEM.

Silicone rubber filled with fumed silicon dioxide gives the image of it fracture surface, which differs from all other studied systems (Fig. 3.8). No clear individual particles are visible at higher magnification either (Figs 3.8b, d). It is obviously caused by two reasons: small size of the filler particles, and a good interfacial adhesion. Reason for the very good interfacial adhesion is the high chemical purity and similarity to the chemical structure of the matrix. The high interfacial adhesion causes that the fracture path does not follow interface, particles on the fracture surface are covered with a layer of matrix, and therefore the fracture

surface is smoother than with the other kind of filler. This kind of fracture surface morphology usually implies rather better mechanical properties. There are only small differences between fracture surfaces of the systems with different filler concentrations (8 phr – Fig. 3.8, 2 phr – Fig. 3.10). The small differences can be interpreted by small inter-particle distances with the systems containing very small particles.
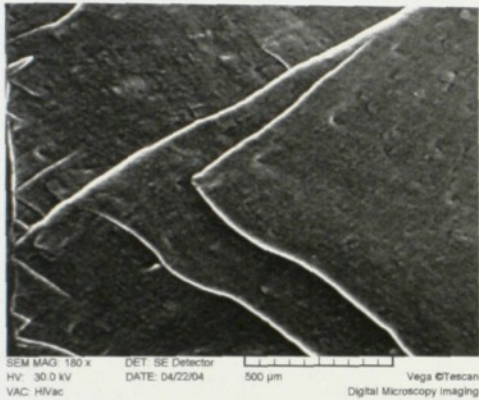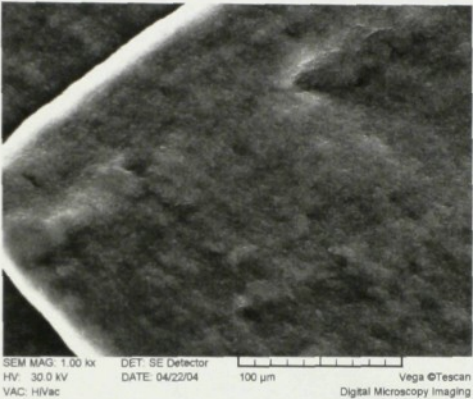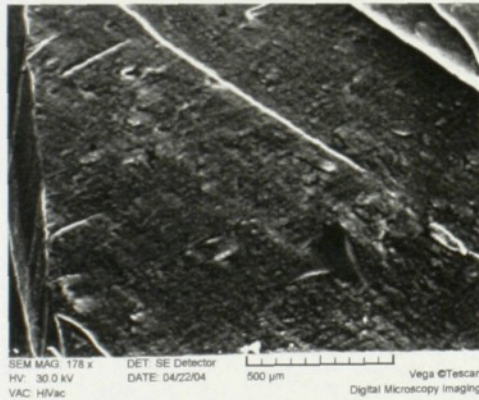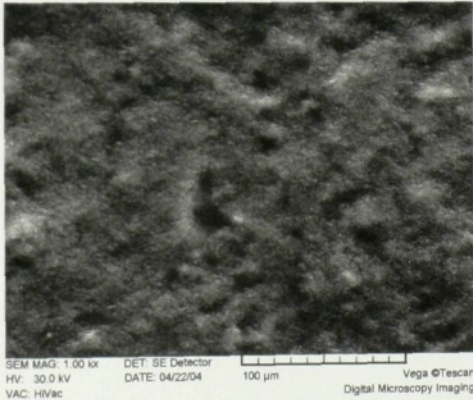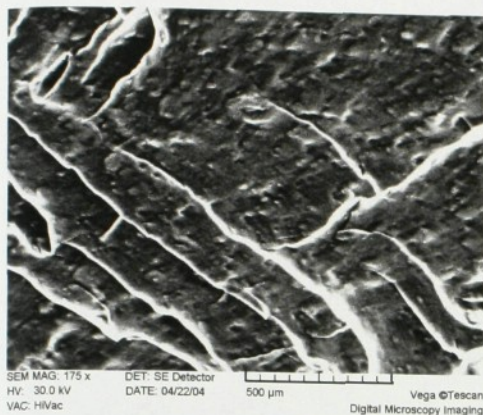

Fig. 3.8a [6683]

Fig. 3.8b [6682]

Fig. 3.8c [6685]

Fig. 3.8d [6684]

Fig. 3.8 Fracture surface of silicone rubber with 8 phr of fumed silicon dioxide. Place close to one surface (a, b), and a place close to the other surface of the sample (c,d). SEM.

Fig. 3.9a [6698]
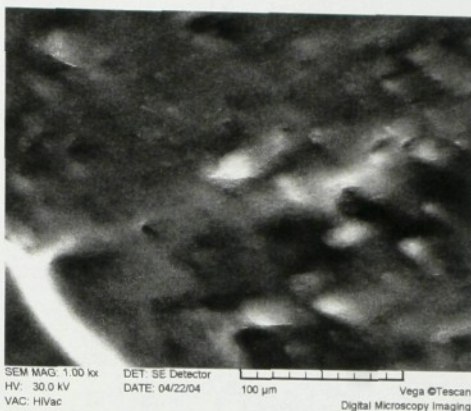
Fig. 3.9b [6697]

Fig. 3.9 Fracture surface of silicone rubber with 2 phr of fumed silicon dioxide. The same place close to one surface. SEM.

Silicone rubber with precipitated silicon dioxide has its fracture surface much more ragged than that with the fumed silicon dioxide (Figs 3.10, and 3.11). Individual particles or rather small aggregates influence the smaller parts of the fracture surface that are otherwise rather smooth. At higher magnification it can be seen that particles act as secondary fracture centres (Figs 3.10, and 3.11 (b) and (d)). Lower filler concentration manifests itself in more pronounced action of individual smaller aggregates as secondary fracture centres (Figs 3.11 (b) and (d)). Big aggregates (c.f. Table 3.1) were not observed on the fracture surfaces, as there are only rare.
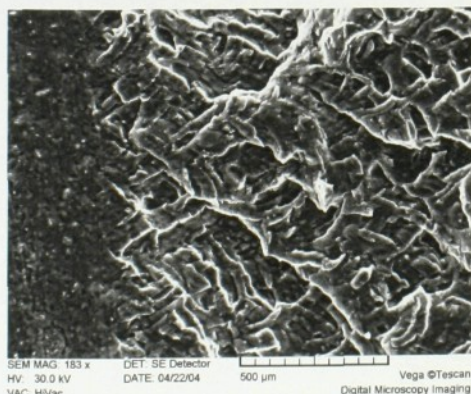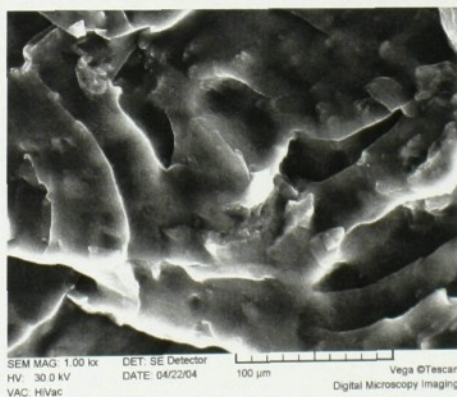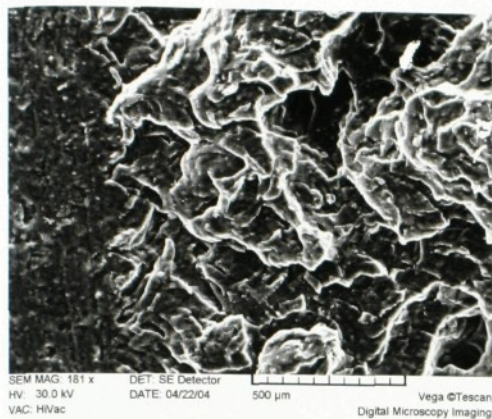
Fig. 3.10a [6688]

Fig. 3.10b [6687]
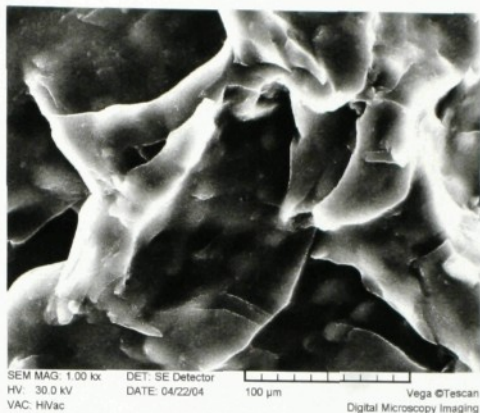
Fig. 3.10c [6690]

Fig. 3.10d [6691]

Fig. 3.10 Fracture surface of silicone rubber with 8 phr of precipitated silicon dioxide.
Place close to one surface (a, b), and a place close to the other surface of the sample (c,d).
A part of notch is seen left in (a) and (c). SEM.
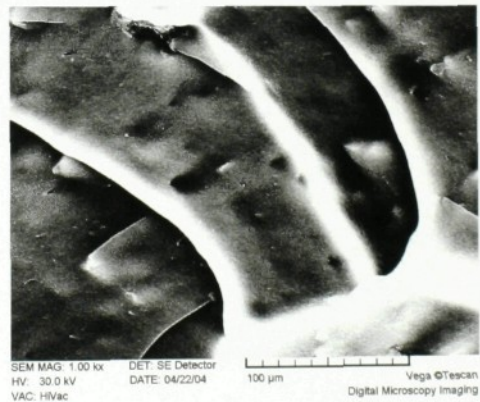

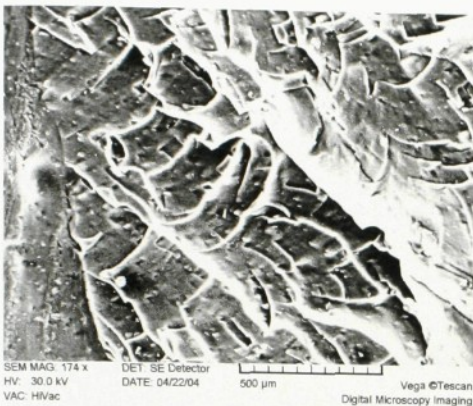Fig. 3.11a [6692]

Fig. 3.11b [6691]

Fig. 3.11c [6694]

Fig. 3.11d [6693]

Fig. 3.11 Fracture surface of silicone rubber with 2 phr of precipitated silicon dioxide.
Place close to one surface (a, b), and a place close to the other surface of the sample (c,d).
A part of notch is seen left in (a) and (c). SEM.

Fracture surfaces of the silicone rubber filled with montmorillonite (Figs 3.12, 3.13) does not show visible sedimentation of the filler at the bottom of the mould from the fracture surface either: density of particles on the fracture surfaces observed at one surface of the sample is almost identical to that at the other surface. This holds for both 8 phr and 2 phr filler concentrations. Comparison of Figs 3.12b, 3.13b shows different filler densities in both cases, and also allows measurements of filler particles or their aggregates.
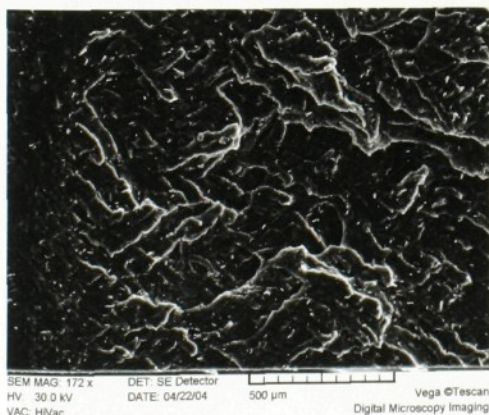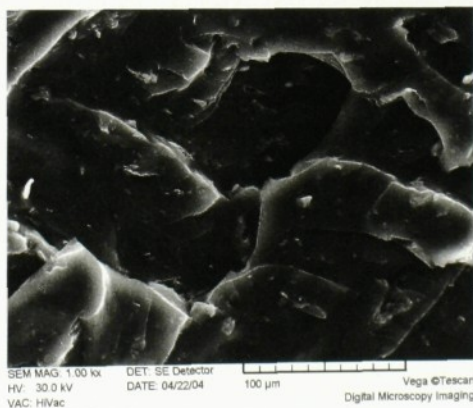

Fig. 3.12a [6681]

Fig. 3.12b [6680]

Fig. 3.12 Fracture surface of silicone rubber with 8 phr of montmorilonite. Place close to one surface. A part of notch is seen left in (a). SEM.
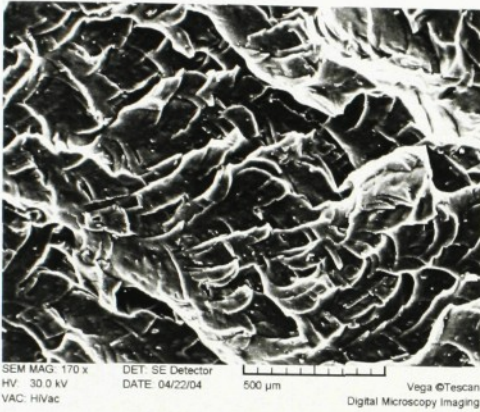

Fig. 3.13a [6700]

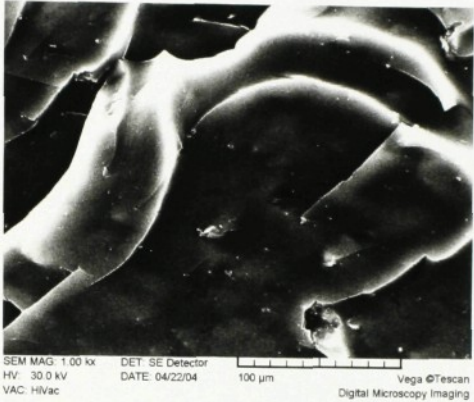Fig. 3.13b [6699]

Fig. 3.13 Fracture surface of silicone rubber with 2 phr of montmorilonite. Place close to one surface. SEM.

Silicone rubber filled with glass bubbles shows a bit different image of the fracture surface. The surface is very ragged compared to other samples containing the same amount of filler (8 phr in Fig. 3.14a). High portion of filler is documented also on the cut surface (Fig. 3.14b). It is necessary to mention here that morphologically we observe volume portions of the filler while the sample contains weight portions. Glass bubbles have low density (600 kg/m^2; c.f. Table 2.1), the other filler used have densities $3 - 4$ times higher. Therefore, the volume portion of glass bubbles in the matrix is also about $3 - 4$ times higher compared to the systems with the other fillers.
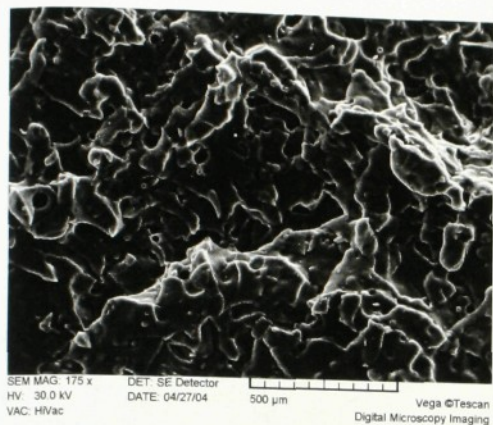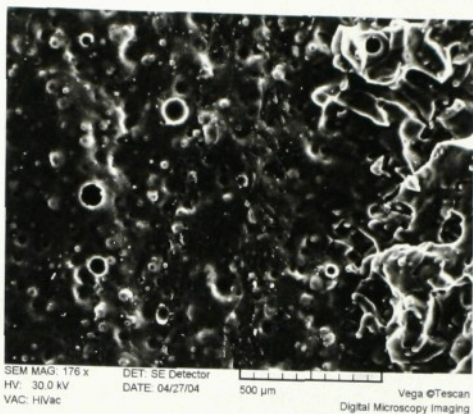
Fig. 3.14a [6769]   Fig. 3.14b [6767]

Fig. 3.14 Fracture surface of silicone rubber with 8 phr of glass bubbles, beginning of fracture path (a), and cut surface in the place of notch with the beginning of the fracture path (b). SEM.

3.3. STRUCTURAL INTERPRETATION OF MECHANICAL MEASUREMENTS

To interpret mechanical measurements together with the help of information obtained from all kinds of microscopy, it is necessary to take into account the following:

- Filler concentration (by volume) points to the data on modulus.
- Filler particle size implies the mean inter-particle distance. Depending on it, deformation mechanism in micro-regions (crazing, shear yielding) influences the absorption of mechanical energy during deformation. [22]
- Size of the particles (including their aggregation) influences the stress distribution around them. Resulting influence is on the ultimate characteristics (strength, extensibility, energy absorption).
- Big aggregates present in the system act as stress concentrators and lower distinctly all the strength characteristics.
- Interfacial adhesion between particles and the matrix influences transfer of the acting force through the material. Low interfacial adhesion can become a nucleus of the fracture crack. Low interfacial adhesion is manifested by spreading the fracture crack along the interface and particles are clearly seen on the fracture surface.

From all the mechanical characteristics obtained (Figs. 3.2 – 3.4) it can be seen that for the silicone rubber the best filler from all the studied is fumed silicon dioxide. Its particles are the smallest, the interfacial adhesion as seen from fracture surfaces is the highest, aggregation, or particle sedimentation does not take place. These parameters have the influence on strength and modulus of the system. Extensibility of the system is also the best from the studied systems but not much higher. Limits of it are probably given by the crosslinking density together with the interfacial adhesion.

The opposite case is the system with quartz sand, mechanical parameters of which are the worst. Reasons are obviously in the biggest particle size, lowest interfacial adhesion, sharp particle edges, narrow particle distribution (no small particles present), and a noticeable particle sedimentation (not an even distribution throughout the sample). All these factors negatively contribute to the measured properties.

The second best system according to the particle size could be expected the montmorillonite-filled silicone rubber. Fracture surfaces, however, show low interfacial adhesion and presence of some (not big) aggregates. Those factors (low interfacial adhesion is probably the more influencing) placed the systems between the average systems.

Bigger particle size than in fumed silicon dioxide is probably the reason why the system with precipitated silicon dioxide yields lower mechanical values placing the system in the "mean". One would expect that the big aggregates (few of them) present in the system lower particularly the strength of the material. Low extensibility is probably the reason of the aggregates present.

Glass flakes exhibit surprisingly low interfacial adhesion to the silicone rubber. Together with extensive aggregation, it pushes the system rather close to the worst one (sand-filled). Fracture surfaces show small holes at the glass-flakes particles, obviously formed during fracturing. This is in agreement with the very low strength and the low extensibility.

Glass bubbles, having higher volume content of the filler as mentioned above, belong to the "mean" as far as modulus and strength is concerned. From that point of view, higher modulus could be expected than measured. On the other hand, this system exhibits relatively very good extensibility.

Explanation of the mechanical behaviour of the studied systems given above cannot include all the details both of the structure aspects and the mechanical behaviour. The extent of the study did not allow sufficient precision in sample preparation, extent in the number of

the test pieces made and measured, and more detailed study of the phase structure of the systems. Additional studies are therefore desirable.

3.4 SWELLING

The inspection of material behaviour on the base of its swelling in an organic solvent was selected purposely because the same elastically active chains of the molecular network play a role during swelling as during deformation. This effect correlates swelling with deformation properties of polymeric network. Swelling is the physical process, where the parts of macromolecular chains between cross bonds are straightened because of solvent molecules, which fill in the places between chains. The crosslinked polymers are insoluble and the polymer network swells only to a limited extent. It absorbs certain amount of solvent and the swelling equilibrium is maintained. The network expands during swelling, and becomes to be deformed in three dimensions. The network chains are being elongated to less probable conformations. Filling the crosslinked polymers influences the ability of systems to swell: degree of swelling of filled elastomeric systems is not generally the same as the swelling degree of corresponding non-filled systems. If there are fillers with small adhesion to the polymer, the polymer chains are teared away from the filler particle surface and the newly aroused places are filed with solvent molecules. With active fillers, the adhesion is too strong and macromolecular segments stick to the surface of filler particles, so that the polymer layer near particles are not swelling to such an extent as the distant layers. [3, 28]

Swelling data are in Figs 3.15 – 3.17. As some curves in Fig. 3.15 overlap, values are repeated in Table 3.2.

From the results of swelling kinetics (Fig. 3.15), the best system is that with the fumed silicon dioxide, as it accepts (absorbs) the smallest solvent quantity. The network obviously remains homogeneous, is not ruptured, the solvent stays inside the matrix and does not break the adhesion of the polymer chains to the filler. On the other hand, the system with the quartz sand appears the worst: the particles seem to promote localisation of the solvent in their vicinity, which fact implies breaking particle-matrix adhesion. Sample cracking in the whole sample volume can be observed with naked eye.
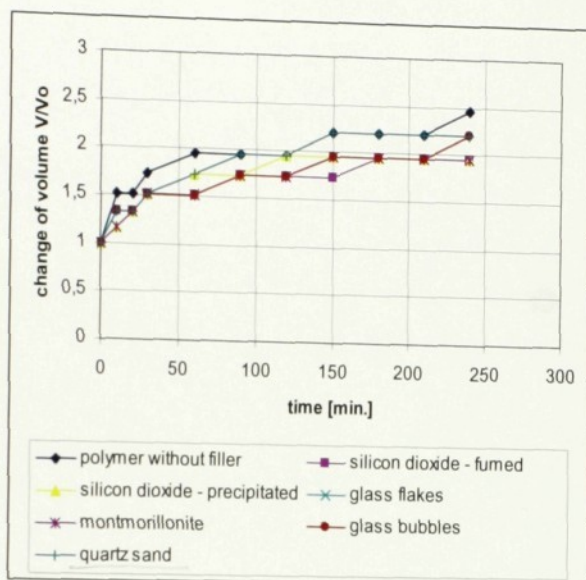
Fig.3.15 Time dependence of volume changes in chlorbenzene of silicone rubber filled selected fillers to 8 phr. Some curves overlap, measured values are in Table 3.2.

Table 3.2 Time dependence of volume changes in chlorbenzene of silicone rubber filled selected fillers to 8 phr.

Time [min.]	0	10	20	30	60	90	120	150	180	210	240
Polymer without filler	1.00	1.52	1.52	1.73	1.95	1.95	1.95	2.20	2.20	2.20	2.46
Silicone dioxide – fumed	1.00	1.33	1.33	1.52	1.52	1.73	1.73	1.73	1.95	1.95	1.95
Silicone dioxide – precipitated	1.00	1.16	1.33	1.52	1.73	1.73	1.95	1.95	1.95	1.95	1.95
Glass flakes	1.00	1.16	1.33	1.52	1.52	1.73	1.73	1.95	1.95	1.95	1.95
Montmorillonite	1.00	1.16	1.33	1.52	1.52	1.73	1.73	1.95	1.95	1.95	1.95
Glass bubbles	1.00	1.33	1.33	1.52	1.52	1.73	1.73	1.95	1.95	1.95	2.20

quartz Sand

Dependence of the swelling kinetics on filling is in Figs 3.16, and 3.17. With the best filler (fumed silicon dioxide), the quantity of the absorbed solvent depends on the degree of filling. However, this dependence is not much pronounced.
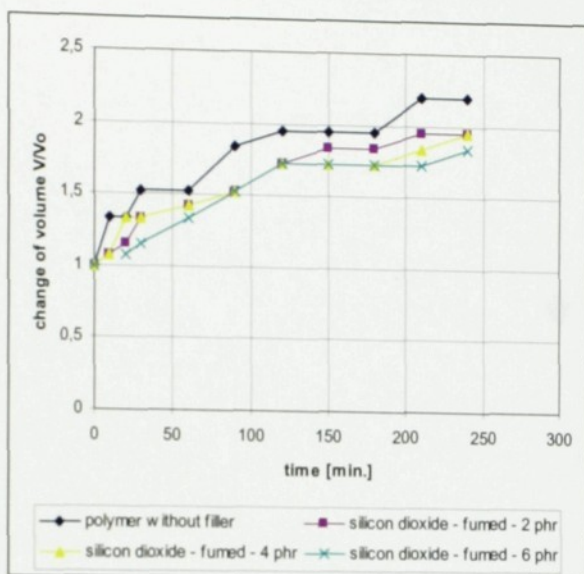
Fig. 3.16 Time dependence of volume changes in chlorbenzene of silicone rubber filled with the best filler to 2, 4, and 6 phr.
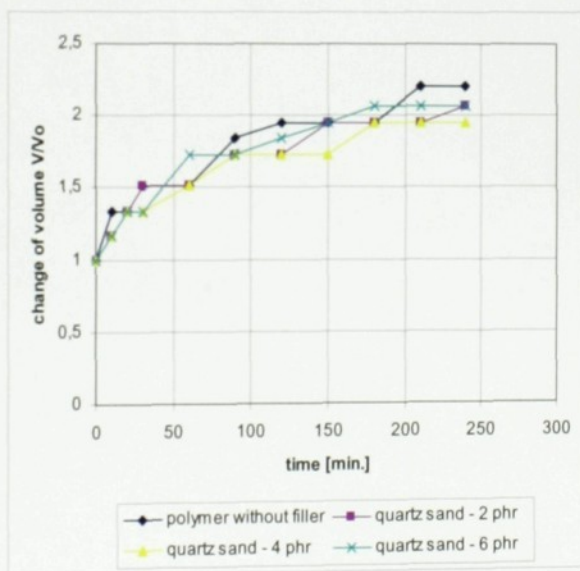

Fig.3.17 Time dependence of volume changes in chlorbenzene of silicone rubber filled with the worst filler to 2, 4, and 6 phr.

4 CONCLUSIONS

- Silicone rubber filled with six inorganic fillers were prepared, concentration of the fillers being 2, 4, 6, and 8 weight percent.
- Stress-strain curves were measured.
- Scanning electron microscopy of fracture surfaces obtained at room temperature was observed (SMFS technique).
- Swelling kinetics in chlorbenzene was measured.
- Mechanical parameters were interpreted on the basis of phase structure information obtained from microscopical observations.
- From the fillers used, the best one is fumed silicon dioxide. The best mechanical data were explained by the smallest particle size, their uniform distribution in the matrix, and the best interfacial adhesion that is a result of high filler purity, and its chemical similarity to the matrix.
- The worst filler is quartz sand. Its influence was explained by the biggest particle size, very low interfacial adhesion, and sedimentation of the particles during the matrix polymerization. The particle size has a predominating effect on the mechanical properties.
- Aggregates of filler particles were observed in the systems with precipitated silicon dioxide, and with glass flakes. In the latter, the aggregation reaches a high extent. Particle aggregation deteriorates substantially the mechanical properties of the systems.
- Sedimentation of particles was observed in the samples with the quartz sand, and sedimentation of aggregates in the samples filled with the glass flakes. Filler sedimentation also deteriorates the mechanical properties of the systems.
- Relatively flat dependences of extensibility on filling remain open to further studies.
- Swelling data correspond with those obtained from microscopical observations and agree with mechanical parameters of the measured systems.

5 REFERENCES

[1] http://www.teachingplastics.org/hands_on_plastics/intro_to_plastics/teachers.html

[2] Epel, J.N.; Margolis, J.M.; Newman, S.; Seymour, R.B.; Eds. Engineered Materials

Handbook, Volume 2: Engineering Plastics, ASM International: 2000.

[3] Gedde, U.W. Polymer Physics, Chapmann & Hall: London, 1995.

[4] Domininghaus, H. Plastics for Engineering, Hanser Publishers: Munich, 1993.

[5] http://www.dowcorning.com/content/sitech/sitechbasics/silicones.asp

[6] http://www.vestaweb.com/silicone/silicone_properties.htm

[7] Schätz, M. Silikonový kaučuk, SNTL: Praha, 1971.

[8] Theocaris, P.S. The Mesophase Concept in Composites, Akademie-Verlag: Berlin, 1989.

[9] CAB-O-SIL Untreated Fumed Silica Properties and Functions, Cabot GmBH, CAB-O-SIL

Division Hanau, Germany, 1993.

[10] Siloxid – vlastnosti a jakostní ukazatele. Silchem, s.r.o.: Ústí nad Labem,1998.

[11] Wichterle, O.; Petrů, F. Anorganická chemie, ČSAV: Praha, 1953.

[12] Antikorozní Pigmenty SILCHEM s.r.o. In The Third International Conference Inorganic

Pigments and Binders. Silchem s.r.o.: Ústí nad Labem, 1999.

[13] http://www.reade.com/Products/Fillers/glass_flake.html

[14] GLASS FLAKES – vlastnosti a jakostní ukazatele. Silchem, s.r.o.: Ústí nad Labem,

1998.

[15] http://www.minweb.co.uk/sheetsilicates/montmorillonite.html

[16] http://www.3m.com/about3m/innovation/glass_bubbles/index.jhtml

[17] Kroisová, D. Ultramikroskopické částice v polymerních kompozitních systémech,

Technical University: Liberec, 2002.

[18] Lukopren N – silikonové kaučuky, Lučební závody a. s.: Kolín, 1998.

[19] Pecina, P. Vliv dotvrzování na pevnostní charakteristiky neplněných epoxidových pryskyřic, Technical University: Liberec, 1999.

[20] Lednický, F.; Michler, G.H. J. Materials Sci., 25, 4549 – 4554, 1990.

[21] Lednický, F. Polymer Bulletin 11, 579 – 584, 1984.

[22] Michler, G.H. Kunststoff-Mikromechanik, Morphologie, Deformations - und Bruchmechanismen, Hanser: Munich, 1992.

[23] Sekutovski, D.G. Fillers and Reinforcing Agents. In: The Polymeric Materials Encyclopedia, CRC Press, Inc., 1996.

[24] Clarson, S.J.; Mark, J.E. Silicone Elastomers. In: The Polymeric Materials Encyclopedia, CRC Press, Inc., 1996.

[25] Tomanek, A. Silicones. In: The Polymeric Materials Encyclopedia, CRC Press, Inc., 1996.

[26] Rolland, P.D.; Matisons, J.G. Siloxane Elastomers. In: The Polymeric Materials Encyclopedia, CRC Press, Inc., 1996.

[27] Hull, D. An Introduction to Composite Materials, Cambridge,1990.

[28] Meissner, B. Fyzikální vlastnosti polymerů, SNTL: Praha, 1971.

6 ABBREVIATIONS AND SYMBOLS

ABS	acrylonitrile - butadiene - styrene
EP	epoxy resin
F	force
GPa	gigapascal
g/cm^2	gram per square centimeter
HDPE	high-density polyethylene
HIPS	high-impact polystyrene
K	degree of Kelvin
kg/m^2	kilogram per square meter
mm	millimeter
mm^2	square millimeter
m^2/g	square meter per gram
MPa	megapascal
N 1000	denotation of material Lukopren N 1000
nm	nanometer
PA	polyamide
PDMS	poly(dimethylsiloxane)
PE	polyethylene
phr	weight amount of filler per hundred weight parts of rubber
PS	polystyrene
PTFE	polytetrafluorethylene
PVC	polyvinylchloride
SBR	styrene-butadiene rubber
SC	surface coating
SEM	scanning electron microscopy
SMFS	soft matrix fracture surface
TEM	transmission electron microscopy
t	time
Tg	glass transition temperature
Tm	melting point temperature

UHMWPE	ultrahigh molecular weight polyethylene
UP	unsaturated polyester resin
UV	ultraviolet
V	measured sample volume
V_0	original sample volume
L	measured length of loaded sample
L_0	original length of sample
R_m	tensile stregth
S_0	original sample profile
A	deformation
wt %	weight percent
°	angular measure; degree
°C	degree of Celsius
α	coefficient of thermal expansion
μm	micrometer
σ	tensile stress
ω	frequency
<	lees than
±	maximum deviation
-	minus; negative ion charge
/	per
%	percent
+	plus; positive ion charge

Declaration

I have been notified of the fact that Copyright Act No. 121/2000 Coll. applies to my thesis in full, in particular Section 60, School Work.

I am fully aware that the Technical University of Liberec is not interfering in my copyright by using my thesis for the internal purposes of TUL.
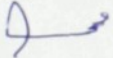
If I use my thesis or grant a licence for its use, I am aware of the fact that I must inform TUL of this fact; in this case TUL has the right to seek that I pay the expenses invested in the creation of my thesis to the full amount.

I compiled the thesis on my own with the use of the acknowledged sources and on the basis of consultation with the head of the thesis and a consultant.

Date

28 - 5 - 2004

Signature