Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych” realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki*

Nanomaterials produced from the gas phase and polymeric nanocomposites

Seminary and Laboratory

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Seminary Part

Introduction to seminars and information about the principles to develop a seminar work

Seminary from the "Nanomaterials produced from the gas phase and polymeric nanocomposites" will be conducted in two person teams ("pair "). The aim of each pair is:

preparation of a literature review on a selected topic, (b) the preparation of key words (max. 6 words), (c) preparation of publication fiches (max. 10 works at the max. 1 book/monograph and 1 for review), (d) preparation of publication fiches in writing (template) and their discussion (seminar paper), (e) preparation the 10 min. presentations on selected topics (they should be prepared in Power Point and registered on CD).

Semniar work:

The assessment basis, in addition to the oral presentation of a chosen topic, will be the seminar paper, which must prepare by each "pair" at the end of course. The aim of this work is presentation of the general state of knowledge, based on literature review for the last 15 years, on a selected topic. A classic layout of the work; i.e. Work title, Authors, Keywords (max. 6), Introduction, Overview of the problem illustrated by relevant charts, diagrams, tables, Summary, Conclusions, and References, is preferred. The volume of the work should not exceed 6 sheets of A4 (font, Times New Roman 12, line spacing 1). The seminar work assessment includes also print of publication fiches, which should be prepared according to the following template:

No.	Authors of the paper
Title of publication	Name of Journal, Vol (Year) Page no.
Keywords:	*max. 6 words*
Research topic:	*max. 50 words*
Research method:	*max. 100 words*
Results:	*max. 100 words*
Conclusions:	*max. 50 words*

For example:

<table>
<tr><td>No. 1.</td><td colspan="2">R. Raj, S.P. Krumdieck</td></tr>
<tr><td colspan="2">A Lanngmuir-Kinetic Model for CVD Growth from Chemical Precursors</td><td>Chemical Vapor Deposition, 19 (2013) 260-266.</td></tr>
<tr><td colspan="3">Key words: Langmuir Absorption isotherms; MOCVD; Processing maps; Step coverage.</td></tr>
<tr><td colspan="3">Research topic: The study of the nucleus growth processes during the chemical vapor deposition of nanoparticles using the Langmuir model.</td></tr>
<tr><td colspan="3">Research method: The classic adsorption model that is described by the Langmuir isotherm was merged with the parameter describing the thermal decomposition of the precursor (the value of this parameter depends on the time).</td></tr>
<tr><td colspan="3">Results: The applied method has been discusse on the example of the TiO_2 layer growth during the CVD processes with the use of 2-propoxide, titanium (IV) as the precursor. The interdependencies between the following three parameters, which describing above problem, i.e. the decomposition reaction rate, the rate of desorption, and the collision rate, can be expressed as a linear sum of the three independent conditions described by the equation "(18)".</td></tr>
<tr><td colspan="3">Conclusions: Results of these investigations revealed the existence of three areas of particle growth; (1) low temperature, wherein the system is controlled by the decomposition reaction, (2) medium-temperature, wherein the reaction rate is slower than the degradation rate of desorption, (3) high-temperature, in which the decomposition of all gaseous phase molecules, which reaching of the substrate surface, was observed.</td></tr>
</table>

Conditions for the course credition:

- The development of keywords, references and publication fiches - ***from 0 to points.***
- Activity in the discussion:
  - Activity during other speaches: ***from 0 to 2 points.***
  - The defense of their theses: ***from 0 to 2 points.***
- The preparation and presentation of the seminar work: ***from 0 to 10 points***.
  - Professional level: **from 0 to 8 points.**
  - The presentation form: **from 0 to 2 points.**
- **Attendance:**
  - **One absence - *requires no justification*;**
  - **The second absence - *subtracting 1 point*;**
  - **More than 3 absence - *0 points and non acceptance of the course.*.**

Seminary Topics (to choose):

1. Fundamentals of kinetic theory of gases.
2. Methods used for the preparation and characterization of surface nanomaterials.
3. The role of the plasma in the deposition process of nanomaterials.
4. Gas phase synthesis of nanopowders.
5. Evaporation Physical Vapor Deposition
6. The physical and chemical deposition from the vapor phase of nanolayers with the participation of plasma.
7. The fabrication of diamonds using CVD methods.
8. The fabrication of metals using CVD methods.
9. The fabrication of metal oxides using CVD methods.
10. Size effects on structure and morphology of nanomaterials.
11. Molecular structure of the surface layer, effects of physical and chemical adsorption.
12. The Arrhenius equation, the dependence of the reaction rate on the temperature.
13. Chemical vapor deposition and atomic layer deposition methods.
14. The thermodynamic theory of nucleation and growth of the layer.

INTRODUCTION TO ISSUES OF THE NANOMATERIALS PRODUCTION FROM THE GAS PHASE

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Fabrication of nanomaterials from the gas phase

Vapour deposition techniques are one of the oldest and most important methods for the preparation of nanomaterials, especially nanolayers, nanocrystals, nanowires, or nanotubes. The general principle of these techniques is vaporization of the material or the chemical compound (which is the source of deposited material) in the vacuum chamber. Physical or chemical processes occurring in the the next stages lead to the nucleation, nanoparticles growth, and the formation of a definite object. In general deposition methods can be divided into: (a) deposition technique, in which the most important role of physical processes, (b) chemical vapour deposition techniques, and (c) techniques based on the pyrolysis processes. The comparison of the deposition rate and surface coverage step for the different vapour deposition techniques is presented in Figure 1.

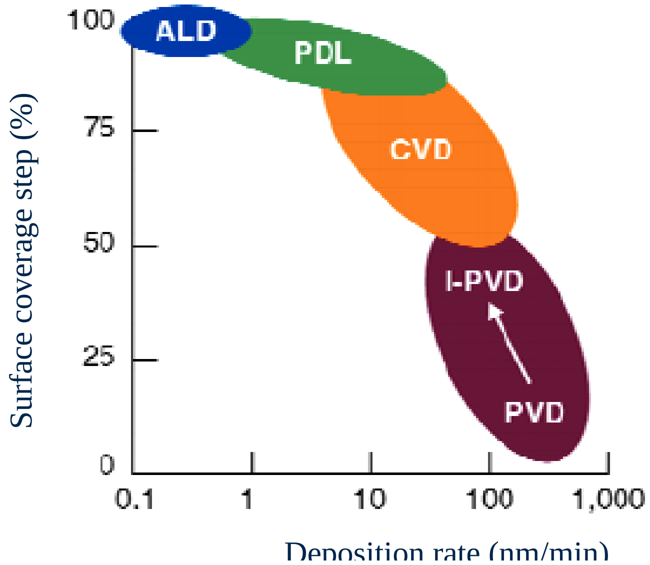

Fig. 1. Dependence between surface coverage step and the deposition rate (PVD – Physical Vapour Deposition, I-PVD – Ionic Physical Vapor Deposition, CVD – Chemical Vapour Deposition, PDL – Pulsed Layer Deposition, ALD – Atomic Layer Deposition).

According to this dependence, the high deposition rates (50-1000 nm / min) and the average percentage of surface coverage (50-70%) are typical for PVD techniques. The degree of the surface coverage is much better when CVD techniques are used and reaches nearly 90%. However, the deposition rate in this case is much smaller and changes from 5 to 200 nm/min. In the case of the ALD technique, the reactants contact takes place only on the substrate surface (gas-phase reactions are eliminated), so that the degree of surface coverage is very high (80-100%). Simultaneously, the typical deposition rate amounts 0.1-3 mm/min.
Classification of vapour deposition techniques:

Physical methods:

- Physical vapour deposition (PVD)
- Cathode sputtering
- Magnetron sputtering
- Vacuum arc deposition
- Laser ablation
- Plasma assistance physical vapor deposition.

Chemical vapour deposition (CVD):

- MO CVD – Metal Organic CVD
- OM CVD – Organometallic CVD
- OM VPE – Organometallic Vapour Phase Epitaxy
- AP CVD – Atmosphere Pressure CD
- UV CVD – UV assisted CVD
- LI CVD – Lasr Inducted CVD
- AA CVD – Aeorosol Assisted CVD
- PA CVD – Plasma Assistance Epitaxy CVD
- PE CVD – Plasma Enhsced Epitaxy CVD

Physical vapour deposition (PVD)

Processes, for which the growth of atomic or molecular layers is obtained by evaporation of the material while maintaining the average vacuum (10^{-4}-10^{-6} hPa) are called as the thermal deposition from the gas phase or physical vapour deposition (PVD). The deposition of thin metallic or non metallc films requires the use of the vacuum system, because in a vacuum, the material boils at a temperature lower than under the normal pressure. In the medium vacuum, the oxidation processes of the boiling surface are reduced and also the number of impurities in the material decreases. The transport of vapors in conditions, in which there is no mutual collisions between molecules is the basic assumption of PVD techniques. Atoms and molecules of vaporized material spread on a straight path from the source to the substrate (Fig. 2.). Physical vapor deposition of materials composed of atoms or molecules (e.g. metal oxides) is not present much difficulty. However, the deposition of materials containing the composite structure is difficult and requires special deposition conditions.

The following steps are important in the formation of the layer:
(a) vapour condensation on a substrate surface,
(b) formation of crystal nucleus,
(c) growth of nucleus and formation of larger crystallites,
(d) coalescence processes,
(e) growth of the layer.

The main factors influence on vacuum deposition process:
- the pressure of residual gas (pressure),
- the rate of evaporation,
- the rate of deposition (growth layer),
- the type of vapour source,
- the temperature of the source,
- the substrate temperature,
- type of substrate,
- mutual position of the vapour source and substrate.

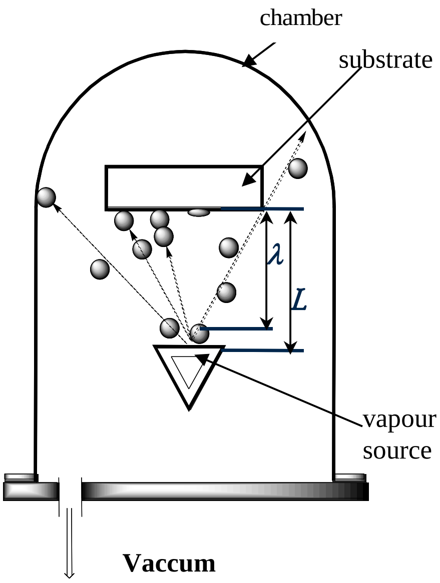

Fig. 2. Scheme of PVD equipment: L – distance between vapour source and substrate, λ - average free path.

Mentioned above factors are interrelated and directly influence on the structure of produced films, their electrical and mechanical properties.

The purity and fine-granularity of received films are associated with the increase of the deposition rate and the decrease of the pressure. Mechanical stresses depend mainly on the substrate temperature and thickness of films. The type of the vapour source, the distance between source and substrate, and the substrate size are main factors, which influence on the thickness of the layer, and also on uniformly coverage of the substrate surface. The structure and layer properties depends on such parameters as the deposition rate, the type of vapour source, the mutual position of the source and the substrate, and the pressure of the vacuum chamber.

The disadvantage of PVD technology is low efficiency of the deposition process, the difficulty of the control of process parameters, and not always the adequate adhesion of deposited layers. The fabrication of uniform layers, well-fitting to the surface shape of the object with complex shapes is the next group of constraints in the wider application of PVD technique in nanotechnology. Another problem relates to the application of this technique in order to the formation of materials with a more complex structure than layers of the metals. In this case, thermal decomposition of the material source, which may proceeds during its evaporation influences on the structure and stoichimetry of the deposited layer. For example, during the evaporation of $BaTiO_3$, this compound partially decomposes forming BaO and TiO_2. The difference in vapor pressure of both oxides causes that the top layer of the substrate will be deposited mainly by BaO but the surface of the $BaTiO_3$ coating will be covered by TiO_2. Only fragmentary reaction of these two components, during the annealing of the layer in an air at the temperature range 1300-1400 K, leads to the formation of the $BaTiO_3$ covers; however cracks and defects on their surface are formed. In order to eliminate these material defects, a new method has been offered the cathode sputtering (ion-sputtering). Technique of the sputter deposition is also carried out in a vacuum chamber, using a low vacuum of about 10^{-2} mbar. The deposited material is placed at the target (cathode) and the substrate is fixed on the anode (positively charged electrode). Resputtering is re-emission of the deposited material during the deposition process by ion or atom bombardment. Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV (100 000 K). The sputtered ions (typically only a small fraction (order 1%) of the ejected particles are ionized) can ballistically fly from the target in straight lines and impact energetically on the substrates or vacuum chamber (causing resputtering). Alternatively, at higher gas pressures, the ions collide with the gas atoms that act as a moderator and move diffusively, reaching the substrates or vacuum chamber wall and condensing after undergoing a random walk. The entire range from high-energy ballistic impact to low-energy thermalized motion is accessible by changing the background gas pressure. The sputtering gas is often an inert gas such as argon. For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target, so for sputtering light elements neon is preferable, while for heavy elements krypton or xenon are used. Reactive gases can also be used to sputter compounds. In such cases, the oxide layers having the precisely defined structure and stoichiometric composition will be formed. This technique is used in fabrication of thin tantalum oxide layers (Ta_2O_5) and such semiconductor materials, as SnO_2, In_2O_5, Ga_2O_5. Sputtering rate depends on: (a) the cathode voltage drop, (b) ion current density in the plasma, (c) the distance between the electrodes, and (d) the type of the sprayed material.

In plasma-assisted deposition methods the activation energy necessary for the initiation of chemical reactions is transferred via charged particles. Due to this fact in many cases the process temperature can be kept small, if gas discharges at pressures below 1 hPa are used. However, processes at atmospheric pressure are more favourable. Basis for a new plasma-assisted deposition method at atmospheric pressure are barrier discharges. Those discharges consist of a large number of transient microdischarges in parallel which are distributed statistically on the surface to be coated. Starting with some basic considerations on the repetitive generation of microdischarges, the deposition of thin polymeric films on glass surfaces is described, using barrier discharges at atmospheric pressure and acetylene.

Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is one of the most important techniques used to fabrication of nanolayers and coatings of inorganic materials of various composition. In contrast to the PVD technique during the chemical vapor deposition (CVD) one or more volatile precursors are transported by the carrier gas to the reaction chamber, where are thermally decomposed on a heated substrate surface. Metals and different multi-element systems (e.g. oxides, sulfides, nitrides, carbides, etc.) having a specific structure, surface morphology and physicochemical properties are the results of the deposition. General scheme of the CVD process is presented in Figure 3.

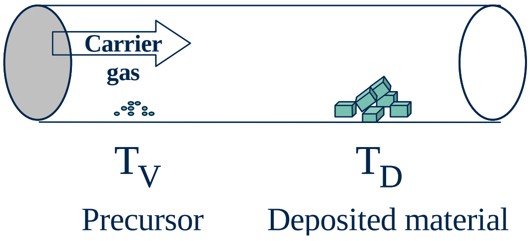

Fig. 3. The chemical vapour deposition scheme.

CVD process can be divided into following stages: (a) transport of precursor vapors by the carrier gas from the vaporizer to the reactor chamber, (b) adsorption of the precursor on the substrate surface, (c) the chemical processes occurring on the surface of the substrate associated with the nucleation and growth of the layer, (d) the formation of by-products, (e) desorption of by-products, (f) their removing from the reactor chamber. The way of CVD processes, structure and physicochemical properties of formed nanoobjects depend on many different factors. The most important are: the geometry of the reactor chamber, the precursor delivery method, the total reactor pressure, the temperature of the substrate, substrate properties, composition and homogeneity of the carrier gas, flow rate, the surface of the substrate, deposition time, the reactivity of the carrier gas, the deposition velocity, and thermodynamic and kinetics properties of all compounds entering the reactor. The number and the type of volatile species transported in vapors, which arrive to the substrate surface, and also physicochemical processes which proceed on the substrate surface, are another factors that must be know leading the CVD process.

In conventional CVD processes (precursor thermolyses proceeded on the surface of heated substrate in the temperature range 473-1073 K) two main reactor types are used: (a) hot-wall and cold-wall reactors. In hot-wall reactors, substrate and the chamber walls are maintain at the same temperature, while in cold-wall one, the substrate is maintained at higher temperature than the reavtor walls. Examination of the deposition rate dependence as a function of temperature enables the study of deposition processes (Fig. 4.). This dependence can be divided in three regimes:

I. Kinetic control – at low temperatures, the growth rate is surface-reaction limited. This is the case when the feed rate is sufficiently high and diffusion limitations do not occur.

II. Diffusion control – the deposition rate is diffusion and/or mass-transport limited. All the reactants that reach the substrate decompose. The reaction proceeds more rapidly than the rate at which the reactant is supplied to the surface by diffusion through the boundary layer.

III. Desorption or prereactions – at higher temperatures, the deposition rate tends to decrease of an increased desorption rate of layer precursor or components, together with depletion of reactants by reaction at the reactor walls.

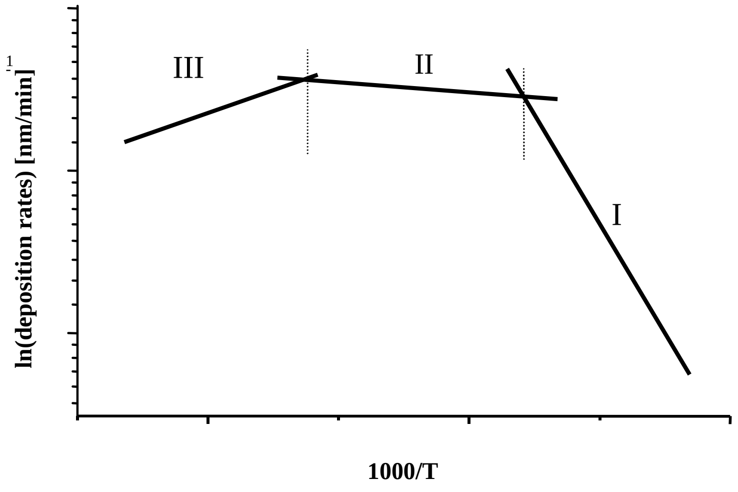

Fig. 4. The deposition rate as a function of the substrate temperature.

From the CVD process point of view, the most important is kinetic regime (I) in which the deposition rate is limited only by the speed reactions occurring on the surface of the substrate. Studying the CVD process it pathway, it can be seen that the precursor is the main factor that affects on the deposition process and the structure and properties of the formed layer. The type of chemical compound, the ligand properties, the type of metal-ligand interactions, and the pathway of precursor thermal decomposition are important. The last factor leads to the formation of clean layers on the substrate surface, with well-defined polycrystalline structure and properties. A chemical compound, which applies as a CVD precursor, must fulfill several conditions. The most important are:

- the volatility of the compound used as a precursor should be sufficient to obtain the possible high-speed transport and high deposition rates respectively, while maintaining the smallest intermolecular forces in the condensed phase and blocking the effects of particle aggregation,
- it should be characterized the high purity, which reduces pollution deposited layers,
- thermal stability of these compounds should be enable to avoid premature precursor decomposition during it evaporation and transport in the gas phase,
- thermal decomposition of the precursor must proceeds with the formation of desired materials, moreover it should characterized the possible lowest content of impurities,
- the formed by-products must have a sufficient thermal stability, and should be easily removed from the reactor chamber,
- precursors should be characterized the low toxicity, the high ignition temperature and the low chemical reactivity,
- precursors should be derived from inexpensive and simple synthesis, to achieve high performance by using inexpensive and readily available reagents.

The types of chemical compounds used as CVD precursors:

Inorganic compounds – e.g. MCl_4 (M =Ti, Zr, Hf) i TiI_4 (CVD of metal oxide); the low volatility, high decomposition temperature (> 773 K), and the necessity of the use of oxidizing or reducing agents (e.g. H_2, SiH_4, H_2O_2).

Metalorganic compounds – e.g. transition metal complexes with alkyl ligands $(M(CH_3)_2$ (M = Zn, Cd), gold(I) and gold(III) complexes with C-diketonates and trimethylphosphanes), cyclopentadienyl ligands (e.g. iron(II) compound - $Fe(h_5\text{-}C_5H_5)_2$), transition metal carbonyls (e.g. Cr ($Cr(CO)_6$ - Cr_2O_3, CrO_2), W ($W(CO)_6$ - WO_3). These type precursors characterized by high volatility and thermal stability, their high reactivity with oxygen can lead to spontaneous combustion.

Metal-organic ligand compounds – e.g. transition metal complexes with β-diketonates ($M(acac)_2$ (M = Ru, Co, Pt, Cu, Ir), $Zr(acac)_4$ (acac = acetylacetonate); these compounds requires the use of a reducing (H_2) or oxidizing (O_2) agent. Alkoxides of transition metals and their complexes with bidendate ligands (e.g.. $M(OR)_n$ (n = 4, 5, M = Ti, Zr, Ta), $OV(OEt)_3$; hydrolysis processes accompanying the thermal decomposition of metal alkoxides can have an adverse impact on the purity of formed layers.

Atomic layer deposition (ALD)

There are numerous CVD-related deposition techniques with widespread applications. These include atomic layer deposition (ALD), also called atomic layer epitaxy (ALE). ALD technique is used for the controlled deposition of monolayers. The film is grown one atomic layer at a time, and the deposition process is based on alternating chemisorption of the different precursors and their surface reaction. Repetition of the growth cycle leads to the formation of controlled layer-by-layer film. An important feature of this process is that the gas-phase precursors do not have contact with each other, they react only on the surface of the adsorption layer. Adsorption and desorption of atoms or molecules on the substrate surface are described by the Langmuir model. The precursor chemisorbs only to active sites on the substrate until all sites are occupied. When carried out within temperature limits, ALD is a self-limiting deposition process.

Advantages of ALD technique:

- Possibility of self-limitation process of layer growth, the number of cycles allows for precise control of material thickness.
- Contact the reactants takes place only at the substrate, eliminating the gas-phase reactions.

- The rate of layer growth is not dependent on precursor flux homogeneity in time and the substrate; this this causes the preferred precursors characterized by the low sublimation rates.
- It has the potential to grow extremely homogeneous crystalline films over large areas.

The major disadvantage of ALD is that film deposition is much slower than conventional CVD, because the deposition rate is typically limited by the time required for switching from one precursor to the other, which usually requires several seconds.

Application of metal alkoxides as MOCVD precursors

The main factors that have decided of the use of these compounds as precursors in CVD methods are volatility of metal alkoxides, their high purity and thermal decomposition towards the metal oxides. Tetra alkoxides of zirconium (IV) were first precursors used for the preparation of ZrO_2 nanolayers on glass substrates. The study of thermal decomposition pathway has shown that high-quality zirconium dioxide layer was formed by the reaction:

$$Zr(OR)_4 \xrightarrow[523\ K]{} ZrO_2\ (s) + 4(alkenes)\ (g) + 2H_2O\ (g)$$

The layers of Ti, Hf, Y, Dy and Yb oxides have been obtained using the same method under the inert atmosphere (Ar, N_2) at temperatures 473-773 K. However, it should be remembered that pure metal oxide coatings can not always be deposited during the CVD process using metal alkoxides as precursors. Previous studies on the use of $Al_2O^tBu_6$, $Mo_2O^tBu_6$ and $W_2O^tBu_6$ as potential CVD precursors of γ-Al_2O_3, MoO_2, and WO_2 revealed that the thermal decomposition of Mo(III) and W(III) alkoxides proceeds differently. Thermolysis of $Mo_2O^tBu_6$ proceeds at temperatures around 483 K with the elimination of cyclohexanol, cyclohexanone, cyclohexene and cyclohexane mixture and the formation of the stable $Mo_2C_4O_4$ betweem 483 and 823 K. However, at higher temperatures (933-983 K), this compound decomposes to Mo_2C. Thermolysis of $W_2O^tBu_6$ proceeds with the formation of $W_2C_4O_4$, as in the case of molybdenum derivative, but at 1073 K this compound loses CO and forms a layer of metallic W.

The important factor that decides about the use of metal alkoxide as a CVD precursor is the possibility of a sufficiently high vapor pressure produce at around 373 K.

This condition meet $M(OR)_n$ compounds which form mainly the monomeric structure. The tendency of metal alkoxides to aggregation and formation of oligomers, as exemplified are $M(OR)_4$ (R = Me, Et, Bu), can be changed by the application of alkoxide ligands containing branched groups, such as ^tBu, ^iBu, ^iPr for the central ion of valence 4, 5 or 6. However, comparative studies of metal alkoxides showed that in the case of tert-alkoxides of alkali metals, alkaline earth and trivalent metals, monomeric forms were not formed. These compounds form dimers, but their volatility was appropriate for their application as CVD precursors.

The aerosol assistant CVD (AACVD) method is a variation of the classical CVD method that allows the use of the low volatile metal alkoxides. The introduction of the metal alkoxide as a suspension or solution into the reactor chamber and their termolyzis on the surface of a heated substrate is the basis of this technique. This method is especially useful in fabrication of materials based on heterometallic oxides. Complexes of general formula $[M(OSi(O^tBu)_3)_4]$ (M = Ti, Zr or Hf), which proved to be good precursors of oxide precursors MSi_4O_{10}, containing the low deposition temperature (ca. 423 K) are examples.

Another issue is the use of alkoxides in the method of ALD. In this case, the high susceptibility of these compounds to hydrolysis is used. An example is the preparation of titanium dioxide monolayer using titanium(IV) isopropoxide and water or hydrogen peroxide as precursors. Pulse 1 consists of $Ti(O^iPr)_4$ on the substrate surface of activated pre-OH groups. After cleaning the surface of alkoxide particles are not connected with the ground (Pulse 2) are placed on a water molecule (pulse 3). On the surface of the substrate reaction:

$$Ti(O^iPr)_4 + 2H_2O \xrightarrow[573\text{-}973\ K]{} TiO_2\ (\text{anataz}) + 4HO^iPr\ (g)$$

CHARACTERIZATION OF NANOMATERIALS SURFACE

Wherever the properties of a solid surface are important, it is also important to have the means to measure those properties. The surfaces of solids play superior role in a remarkable large number of processes, phenomena, and materials of technical importance. Therefore, quantitative and qualitative analysis of the surface is very important in studies of nanomaterials, however the registration of the analytical signal in the analysis of nano-object surfaces requires very precise techniques. Photons, electrons, ions, neutral particles or electric fields can be the source of the sample excitation. Simultaneously, the information about the sample can be also carried by photons, electrons, ions, neutral molecules, and the electrical, magnetic, acoustic, or thermal interference effects. Because the various types of particles can appear in both primary excitation and secondary emission, about 700 different analytical techniques are used to study the surface characteristics. Among this group, the following methods are the most frequently used:

1. Methods using ions as the source of excitation:
   * Secondary-ion mass spectrometry (SIMS),
   * Rutherford back-scattering spectroscopy (RBS),
   * Glow discharge mass spectrometry (GDMS).
2. Methods using electrons as the source of excitation:
   * Scanning electron microscopy (SEM),
   * Energy dispersive X-ray spectroscopy (EDX),
   * Transmission electron microscopy (TEM),
   * Selected area electron diffraction (SEAD TEM)
   * Auger electron spectroscopy (AES),
   * Low-energy electron diffraction (LEED),
   * Electron energy loss spectroscopy (EELS),
3. Methods using photons as the source of excitation:
   * Laser ablation (LA),
   * X-ray diffraction (XRD),
   * Total reflection X-ray fluorescence analysis (XRF),
   * X-ray absorption spectroscopy (XAS),

* Infrared spectroscopy (IR),
* Raman spectroscopy (R),
* X-ray photoelectron spectroscopy (XPS),

4. Methods using mechanical forces:
   * Atomic force microscopy (AFM),
5. Methods using surface electrical properties:
   * Scanning tuneling microscopy (STM).
   * Scanning tuneling spectroscopy (STS).

Electron microscopy enables access to information about the position, chemical state and local electron density for each of atom in a material in all three dimensions. The access to the quantitatively interpretable information on an appropriate length scale (for nanotechnology from ~0.1 nm to few hundreds of nm) has major impact on scientific understanding, the development of new nanomaterials and their applications.

Scanning electron microscopy (SEM), An electron beam is thermally emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to computer data storage.

Atomic force microscopy (AFM) This method is usually used to image and manipulation of atoms and structures on a variety of surfaces. The equipment consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe (see scanning thermal microscopy, scanning joule expansion microscopy, photothermal microspectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Due to the nature of the forces used for imaging the sample surface AFM microscope can operate in either: (a) *Contact mode*: the tip is used as a profilometer examining the topography of the surface (the surface of the blade pressure from 10-7 to 10-11 N N). In this mode, we use short-range interatomic forces, (b) Non-contact mode: the tip is pushing at a distance of 10-100 nm, for imaging use long-range forces, such as magnetic forces, electrostatic and attractive van der Waals forces. In this method, imaging can not measure the static deflection of the lever, but we put the lever in the vibration frequency is close to its resonance frequency using a piezo element, (c) The mode of intermittent contact: in this mode, the tip periodically hits the surface of the sample.

Techniques, which enable the determination of nanomaterials qualitative and quantitative composition, polycrystalline structure and depth profile are the most important in studies of nanoobjects. Measurement of depth profiles is based on detection of the masses of interest during sputter removal of the sample material.

Glow discharge optical emission spectrometry (GDOES): universal technique used for determining the gradient distribution of all elements (including hydrogen) in the surface layer of materials. The source of the information about the type and the number of atoms, which form the sample is ultraviolet, visible and infrared electromagnetic radiation (of range 2000-9000 Å) generated by glow discharge. GODES spectrum is a result of atoms or ions removing of from the substrate surface by the effect of the diode sputtering and their optically induction in acts of collisions with electrons. Analysis of these data enable the obtain information about the sample (optical spectrum), and the digestion profile analysis.

Secondary Ion Mass Spectrometry (SIMS): is a technique used in order to the analyze of materials surface, the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions. These secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface. SIMS is the most sensitive surface analysis technique, being able to detect elements present in the parts per billion ranges.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are currently the most widely used surface-analytical techniques. XPS, also known as ESCA, is the most widely used technique for surface analysis because of the relative simplicity of use and interpretation of data. The sample is irradiated with mono-energetic X-rays causing the ejection of photoelectrons from the core electron levels. The difference between the initiating radiation energy and the energy of ejected photoelectrons (energy of the electron bonding) is characteristic for the individual elements, and this allows for their identification in the sample. For example, energies of electrons are usually included in the range of tens to 1500 eV. Resolution of the XPS method enables simultaneous multi-elemental analysis. Analytical information obtained by XPS corresponds to the surface layer of studied object with a thickness of 0.5 to 3 nm. The information XPS provided for surface layers or thin film structures has a value in many industrial applications, including: surface modification of polymers, catalysis, corrosion, adhesion, semiconductor and dielectric materials, packaging, electronics, magnetic media, and thin coatings applied in many industries.

Auger electron spectroscopy; this method is associated with the phenomenon of Auger electron emission, which is a secondary process in comparison to the photoelectron emission. The surface to analyzed is irradiated with a beam of electrons of sufficient energy, usually in the range 2-10 keV, in order to ionize core levels in surface of atoms. After ionization the atom can relax by two processes - ejection of a characteristic X-ray photon or ejection of an Auger electron. The energy of this electron is a function of atomic energy levels only. According to the above dependency we can state that no two elements that have the same set of atomic binding energies. Therefore, analysis of Auger energies enables the elemental identification of samples. The normal range of kinetic energies registered in an AES method would typically be from 20 up to 1000 eV, corresponding to inelastic mean free path values of 2 to 6 monolayers.

In addition to mentioned above analytical methods, X-ray diffraction (XRD), X-ray energy dispersed spectroscopy (EDX), Raman spectroscopy and also attenuated total reflection and diffuse reflectance infrared spectroscopy (FTIR ATR, DRIFT) are important to the analysis of nanoobjects surface.

TOPICS CONNECTED WITH THE SURFACE PROCESSES AND THE LAYER STRUCTURE

Synthesis of nanoobjects is usually associated with the surface chemistry, and also with the size and shape of particles, which build them. Therefore, at the beginning of the discussion about nanotechnology and nanochemistry, the problems related to the surface notion, determination of surface structure and properties, investigation of the possible surface processes, should be firstly defined. By a surface of the material we mean one or more surface atom layers, separating the interior of the solid/liquid phase from the gas phase or a vacuum.

1. The surface structure

Discussing the problems associated with the system surface, the two inseparable aspects should be taken into consideration, i.e. its electronic and geometric structure. The important feature of nanoscale materials is their surface to volume ratio, which value rapidly increases with diameter decrease (Fig. 5.)

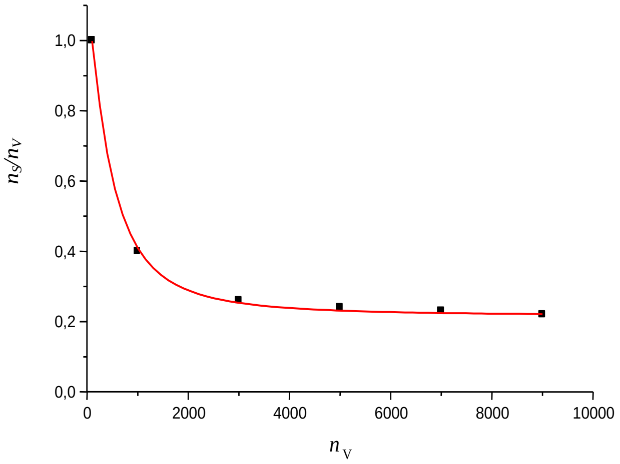

Fig. 5. Changes of n_S/n_V parameter values (n_S – number of atoms on the particle surface, n_V – number of atoms in the particle volume) as a function of atoms number in in the whole volume of the particle.

Number of atoms in the entire volume of the particles, as well as on particles surface can be determined on the basis of unit cell parameters. Moreover, the particle shape can be also known in order to determine its volume. Assuming that particle has a spherical shape, its volume is described by the formula: $V_{sphere} = \frac{4}{3}\pi r^3$. Considering that the unit cell volume is $V = a^3$, we can calculated the number of atoms in the entire volume from the following equation: $n_V = n_{surf}\frac{4}{3}\pi\left(\frac{r}{a}\right)^3$ (where *r* is the particle radius), while the number of surface atoms may be determined from the equation: $n_{surf} = n_{unit}4\pi\left(\frac{r}{a}\right)^2$. For the plane, cylinder or cubic particles above mentioned features can be designated using the formulas for the volume of the particles, respectively: $V_{pl} = al^2$, $V_{cylinder} = \pi a^2 l$, $V_{cube} = a^3$ and surface $S_{pl} = 2l^2$, $S_{cylinder} = 2\pi a l$, $S_{cube} = 6a^2$.

The most important for the characterization of the plane are low-index planes. Low-index planes can be thought of as the basic building blocks of surface structure as they represent some of the simplest and flattest of the fundamental planes. Figure 6. shows two examples of (100) and (111) index planes in the fcc (face-centred cubic) system.

Fig. 6. Hard sphere representation of *fcc* low-index planes: (a) (100) i (b) (111)

For example, the surface of the low-index plane (111) is formed by the cutting of the face-centred cubic crystal (*fcc*) in that way that the plane cut x-, y-, z- axis in the same values. This corresponds to the arrangement of atoms on the surface in a trigonal symmetry system (apparently hexagonal). This type of arrangement of units/blocks on the surface corresponds to a monolayer of the densest packing of the fcc structure.

2.

Characterizing atoms located on the surface of the particle/block/layer, we can assume that they have free unsaturated bonds, which have partial electric charge. Therefore, the energy of atoms, which are located on particles surface is higher then atoms in their depth. Surface energy (γ) can be described by equatation (2):

$$\gamma = n_{surf} \frac{\Phi}{2}$$

(2)

n_{surf} – surface density of free bonds

Φ – bond energy

2. Adsorption and desorption processes

Interpreting the equation (2) we can state that the surface energy increases with the density of free bonds. The composition of the surface, its roughness and curvature, are the main factors affecting the value of the surface energy. The shape of the surface is the next important factor, because it affects on the different density and number of free bonds, and thereby different values of surface energy. Surface energy, determines the way of the system interaction with the environment, which results from its tendency to the energy decrease by the formation of interactions with the environment. Considering the nanotechnology viewpoint, the adsorption processes play a vital role in many applications, e.g. synthesis of solid materials, catalytic processes, solar cells, or chemical sensors. In the description of this phenomenon, the peculiar nature of interactions between adsorbate molecules and the adsorent surface must be considering. These interactions may be of two types, which enables the distinguish two types of adsorption: physical adsorption and chemical adsorption.

Physical adsorption; the forces operating are weak, e.g. van der Waals type. The speed of this process is mainly limited by the diffusion rate of the adsorbate towards the surface. This type of adsorption decreases with increase of temperature.

Chemical adsorption (chemisorption); involves the formation of chemical bonds between the adsorbate and adsorbent is a monolayer. The nature of the interactions caused that this is a specific process, which concerns only some of the adsorbents and certain particles. Chemisorption is an activated process, and its rate dependends on temperature, according to the Arrhenius equation:

$$\rho = k(T)f(c) = A\exp[-E_a(RT)]f(c)$$

where ρ - adsorption rate, $k(T)$ – adsorption rate constant, E_a – aktivation enery, $f(c)$ – concentration function of the adsorbed substance.

Studying the surface processes that occur during the formation of nanolayers, should be noted that only those atoms, which are located on the surface of the substrate and include free bonds can adsorb adsorbate particles. Saturation of these bonds leads to the formation of monolayer. Usually only part of the surface (so called "active centres") is active. Each active center adsorbs only one adsorbate molecule and therefore the maximum adsorption is associated with the filling of all adsorption centers. tThe surface coating size determines the surface coverage degree (θ), whose value changes between 0 and 1:

$$\Theta = \frac{n}{n_{\max}}$$

where; n – number of adsorbed particles, $n_{\max}$ - the maximal number of particles, which can be adsorbed on the surface.

The method that enable the reduction of the surface energy is its functionalization by elimination free bonds. For this purpose, different types of molecules depending to the chemical properties of the surface can be bonded to the substrate surface Fig. 7. The surface functionalization problem should be considered as a molecule-molecule reaction, in which the change of the surface from hydrophilic to hydrophobic is the result of.
The above mentioned phenomena are related to the formation of the so called self-organizing layers, i.e. layers, which are obtained in spontaneous process leading to the formation of three-dimensional systems, composed of several components. This phenomenon occurs in physics, chemistry and biology open systems, which are far from the thermal equilibrium state. The following factors are most important for the formation of self-organizing layers :

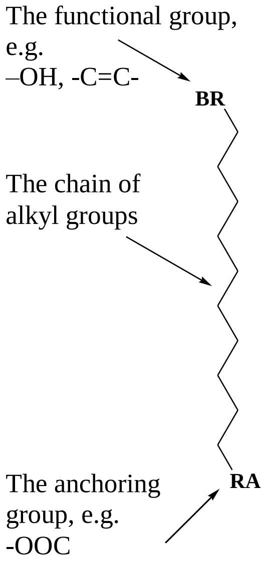

Fig. 7. Functinalization molecule

1. energy parameters defining the formation of bonds between anchoring group and metal,
   as well as non-covalent interactions formed in the organic side groups,
2. parameters determining the position of anchoring group on the metal surface (these prarameters are important for the 3D geometry),
3. the structure of anchoring groups - the organization of the organic layer is the result of intermolecular interactions occurring in the lateral parts of the molecules (van der Waals interaction and hydrogen bonds),
4. influence of side groups and the sterical thickening effect of organic groups.

The following factors influence on the uniform distribution of a chemical compound on the metal surface: (a) the type of solvent, (b) temperature, (c) the concentration of the adsorbed compound, (d) the immersion time of the adsorbent in the solution, (e) the purity of the adsorbate (f) the presence of oxygen in the solution, (g) the properties and the nature of the prepared surface, (h) purity of the substrate, and (i) the length of aliphatic chains.

3. The nucleation and growth of the layer from the gas phase

The increase in the coating from the gas phase is a complex process which successive steps are shown in Figure 8.

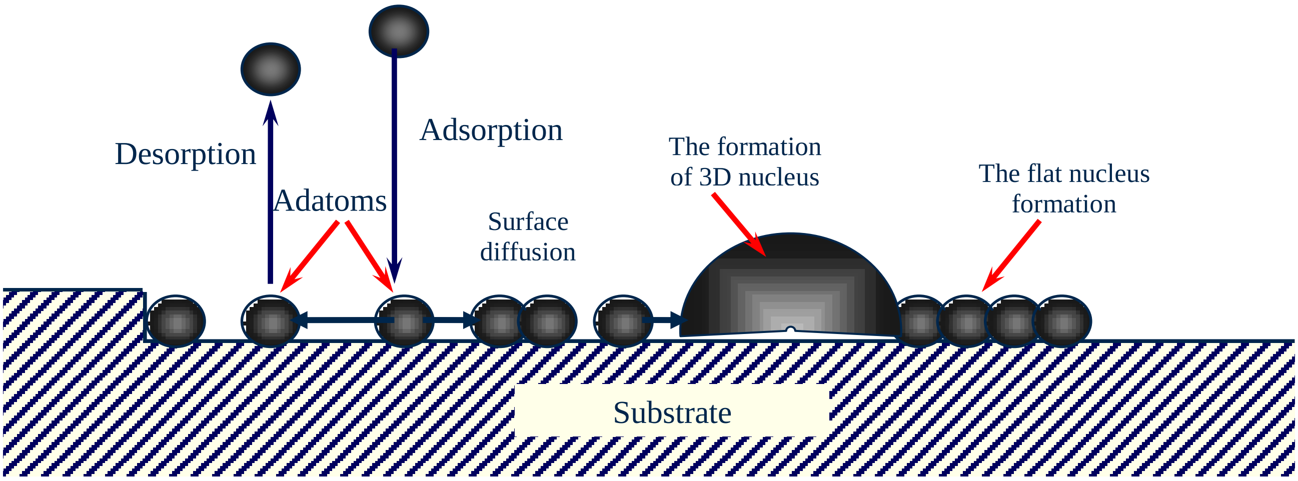

Fig. 8. The main phenomena, which occur on the substrate surface during the particle nucleation and growth from the vapor phase.

The first stage of these processes involves adsorption of precursor atoms/molecules to the substrate, which in successive stages the crystallization nucleus form. On the substrate surface, the equilibrium state between adsorption and desorption processes is formed. Cabera-Zwanzig showed that atoms transfer their energy during elastic collisions with the substrate surface when the energy of the incident particle is not greater than the desorption energy more than 25 times. In the case of the desorption energy of metal atoms is about 0.1-0.5 eV, which means that the adsorption of metal atoms from the gas stream may take place at a temperature no greater than 105 K. At the equilibrium, the life time (t_c) of adsorbed particles can be described by the following relationship:

$$t_c = \frac{1}{v}\exp\left(\frac{E_{desorpcji}}{kT}\right)$$

v – the vibration frequency of adsorbed particles/atoms

Number of atoms/molecules adsorbed on the substrate surface can be described by a following dependence:

$$n_1 = Jt_c\left(1 - e^{\frac{-t_{os}}{t_c}}\right)$$

J – the flux density of particles interacting with the substrate, ***t*** – the time of the coating deposition.

Considering that the deposition time of the layer is much greater than the adsorbed particles lifetime ($t >> t_c$) the dependence, which describe of the number of atoms/molecules adsorbed on the substrate surface can be simplified and presented as:

$$n_1 = Jt_c$$

In the above relation a parameter ***J*** is important, i.e. the value of particles/atoms flux density arriving to the substrate surface. At the equilibrium, the ***J*** parameter is equal to the flux density of vaporized particles/atoms and is described by the relation:

$$J = \frac{p}{\sqrt{2\pi mkT_{pod}}} = \frac{n_1}{t_c} = n_1 v e^{\frac{-E_{des}}{kT_{pod}}}$$

where: ***p*** = the pressure of supersaturated vapor above the substrate surface, $\boldsymbol{T_{pod}}$ = substrate temperature.

Thus, after establishing of the balance between the number of atoms in the gas phase (n^0), and the number of adsorbed atoms (n_1), the following relationship must be satisfied:

$$\frac{p}{p^0} = \frac{n_1}{n^0}$$

wher: $\boldsymbol{p^0}$ – the pressure of supersaturated vapor above crystallized layer.

The particles/atoms adsorbed on the substrate surface can migrate and connect into the larger clusters (formation of polyatomic grains), which can form nuclei of crystals. In the next stage, as a result of the coalescence process these nuclei will form the so-called "islands", growing to a continuous layer (Fig. 9).

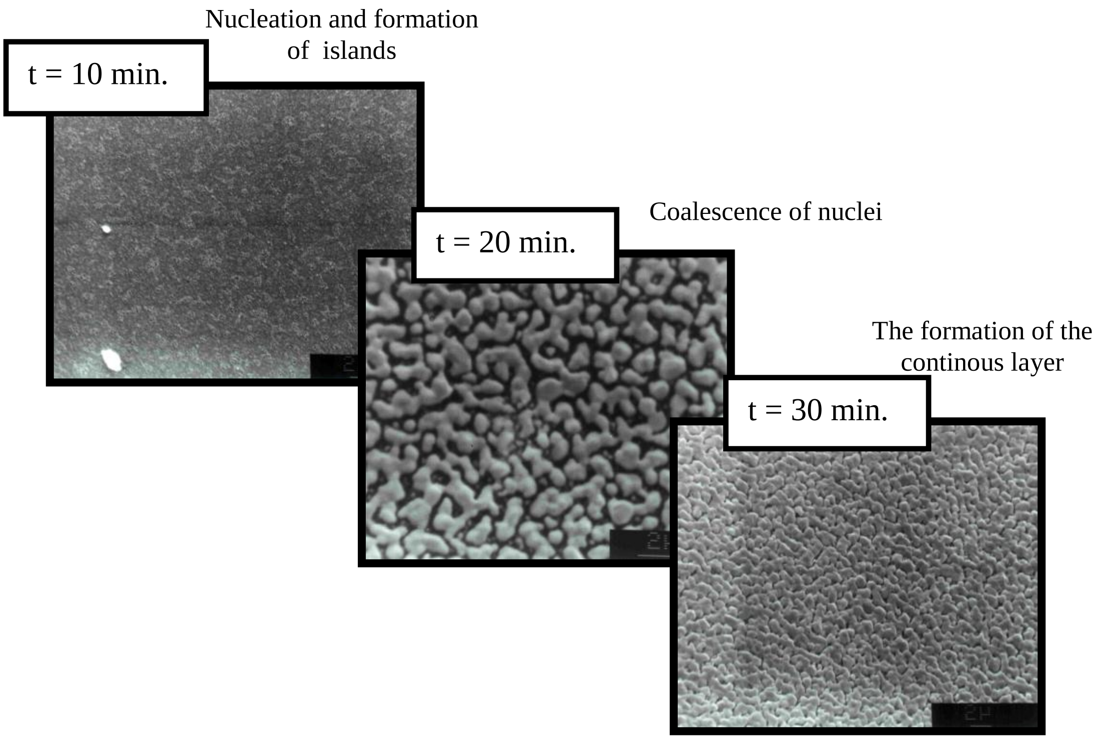

Fig. 9. SEM images of morphology changes of Ag layers in function of the deposition time.

The nuclei can be formed and grows from the gaseous phase only when the the gas phase is saturated with respect to the solid phase. The value of supersaturation express by the relationship:

$$\Delta p = p - p^0$$

Supersaturation value for the specified pressure and temperature can be determined from the equilibrium phase diagrams in the system $p = f(\mathrm{T})$. The thermodynamic driving force of this phase transformation can be presented as a difference between chemical potential of supersaturated vapor μ_g^p and infinitely large crystal μ_K^0:

$$\boldsymbol{\Delta\mu = \mu_g^p - \mu_K^0}$$

Assuming that the saturated steam and supersaturated behaves like an ideal gas, the chemical potentials can be describe the dependencies:

$$\mu_g^p = \mu_K^0 + kT\ln p$$

$$\mu_K^0 = \mu_K^0 + kT\ln p^0$$

Thus

$$\Delta\mu = kT\ln\frac{p}{p^0}$$

the above mentioned dependency shows that the difference of the chemical potential on the border of supersaturated vapor phase and crystal, depends on the supersaturation degree, i.e. the pressure ratio of the supersaturated vapor (p) (p) and saturated (p^0).

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POLYMER NANOCOMPOSITES

Prof. dr hab. Halina Kaczmarek, Dr. Tadeusz Czerniawski

Assessment

The prerequisite is to perform 6 exercises and submission of reports on all completed tasks; Rating - current during exercise and rating reports.

INTRODUCTION

1. Polymer Composites

Polymer composites, also known as polymeric compositions or reinforced plastics, are two-or multi-component systems, wherein the base is a high molecular weight compound, and added modifier changes the physicochemical properties of the initial polymer [1-10]. Most modifying substances applied are fillers which result in the desired change of mechanical strength, impact strength, hardness, heat resistance, or photostability. Other commonly used modifiers may include plasticizers, stabilizers or processing aids. Usually these substances are in solid form, although some of them may also be liquids. Modification also changes other physicochemical properties of the polymer (density, optical, electrical, spectroscopic, surface properties, etc.). Valuable advantage of polymer composites used in practice, it is also sound and vibration damping and low permeability of gases and liquids.

Considering the properties of polymer composites, it is necessary to remember that in most cases, they form the heterogeneous systems due to the thermodynamic incompatibility of components. In this case, a necessary condition of miscibility: $\square G_m = \square H - T\square S < 0$ (where $\square G_m$ represents a change in the thermodynamic potential, i.e. the Gibbs free enthalpy, $\square H$ - change in enthalpy of the system, $\square S$ - change in entropy, T - absolute temperature) is not fulfilled.

In some cases, compatible systems may be formed. They are non-homogeneous at the molecular level, however, are uniform in the macroscale (i.e. the dispersed particle sizes are less than 1 micrometer), and it is often sufficient to improve their utility properties.

Polymer dispersion medium must have the appropriate parameters to enable the processing of composite and exhibit specific interactions and sufficiently good adhesion to the added modifier to achieve the desired properties. The adhesion at the interface is determined by the presence of functional groups in the structure of the components, which may join via dipole or ionic interactions as well as hydrogen bonds.

Typical polymers used for production of composites include:

- thermoplastics (such as polyolefins, polyvinyl chloride, polyamides, polycarbonates), which soften when heated and become more fluid as additional heat is applied. The curing process is completely reversible as no chemical bonding takes place. This characteristic allows thermoplastics to be remolded and recycled without negatively affecting the material’s physical properties;
- thermosetting polymers (e.g. epoxy polymers, unsaturated polyesters, polyester, phenolic, melamine-formaldehyde) are polymers that cross-link together during the curing process to form covalent bonds, thus they undergo hardening. This process (occurring upon heat, irradiation or chemical agents) is irreversible and it eliminates the risk of the product remelting during heating.
- elastomers (natural and synthetic rubbers, vulcanized and unvulcanized polymers, e.g., plasticized polyvinyl chloride), which are polymers with viscoelastic properties (having both viscosity and elasticity) and very weak inter-molecular forces. They are characterized by flexibility in the temperature of use. They can be reversibly deformed under the action of mechanical forces, maintaining the continuity of their structure. They have very low glass transition temperature (much lower than room temperature) and show the tensile elongation greater than 100% (it may be up to 1000% without breakage of the sample).

Thermoset composites are characterized by ease of molding, high stiffness and compressive strength. The disadvantage of these systems is poor impact resistance and low elongation under tension. Similar properties are composites chemically hardened, which need a suitable chemical reagent (called a hardener) for crosslinking. Chemical curing agents are aliphatic and aromatic amines, polymercaptans, anhydrides, and Lewis acids and bases (for example, boron fluoride and tertiary amines).

Unmodified thermoplastics exhibit relatively poor mechanical properties, hence their improvement is required (for instance, by the addition of glass fibers, carbon or ceramic).

However, after such modification, other composite properties are deteriorated (e.g. electrical conductivity).

Among the numerous fillers - fibers (which may be in the form of short filaments or in the form of continuous fibers), the powders (in the form of spherical particles, flakes, etc.) can be listed. Properties of polymer composites depend not only on the structure and the chemical properties of the components but also on the size and degree of dispersion of additive. In the case of the fibers, their orientation is also important. Another type of composite are laminates (layer systems), obtained by pressing of superposed films of various materials such as different polymers, polymer films and metal (often aluminum), polymer film with the fabric.

Taking into account the origin, filers can be classified into synthetic (organic, inorganic) and natural (e.g., starch or vegetable fibers - cellulose, cotton). Among synthetic fillers the following chemicals can be listed: silica, talc, mica, metal oxides (zinc, aluminum, magnesium, titanium), glass (in the form of fibers, beads or bubbles), carbonates (barium, potassium, calcium), carbon fibers and carbon in the form of carbon black or graphite, ceramic fibers (mainly based on Al_2O_3 and SiO_2), metal powders and alloys, polymer reinforcing fibers such as poly-para-aramide type - Kevlar (Fig. 10).

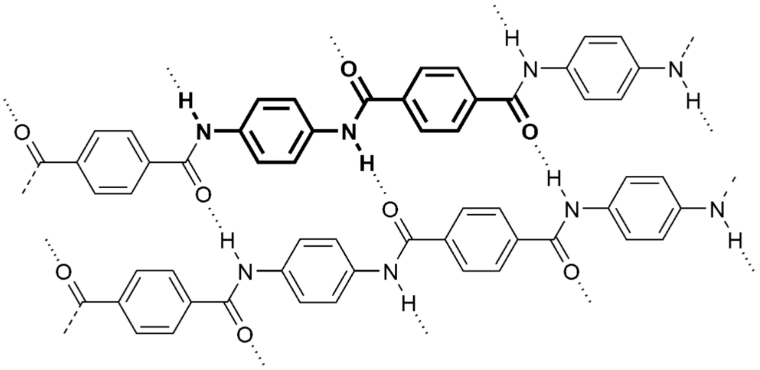


Fig. 10. Chemical structure of poly (terephthalate-1,4-phenyldiamide), PPTA, the trade name Kevlar, developed at DuPont in 1965; bold represents a monomer unit, dashed lines indicate hydrogen bonds [http://pl.wikipedia.org/wiki/Kevlar. 10.07.2014].

We should also mention the possibility of using of waste materials as filler for production of ecological organic composites. For this purpose, a ground tire rubber or recycled poly(ethylene terephthalate) (Fig. 11) that is material from discarded PET bottles for beverages, can be used.

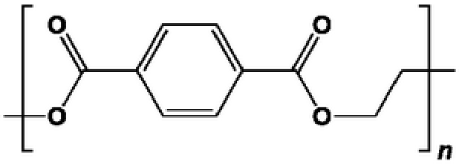


Fig. 11. Chemical structure of poly (ethylene terephthalate), PET.

Modern, durable polymer composites comprise continuous ceramic fibers (aluminosilicate) produced by extraction from the liquid phase, which are then processed by weaving methods. Glass fibers are manufactured from a special grade of aluminoborosilicate glass that is alkali-free (<2%). The smaller the diameter of fibers, the better mechanical properties have reinforced composites. Additional benefits of such organic-inorganic (i.e. hybrid) composites are reduced water absorption and flammability, increased resistance to microorganisms and aging, high thermal and chemical resistance. Inorganic fibers have replaced the carcinogen asbestos used in construction quite common even in the last century.

Glass fibers reinforcing polymers should be surface-modified. Usually for such modification, the coupling agents, which have two different functional groups in the molecule, are applied. One of these groups is covalently bound to the polymer, the second – combines with fiber (Fig. 12). This requirement fulfills silicone, titanium and chromium compounds.

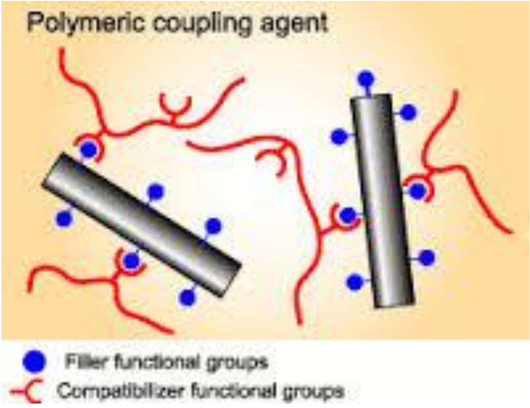


Fig. 12. Mechanism of binding of the glass fibers to the polymer via a coupling compound [http://www.specialchem4polymers.com/tc/adhesion-promoters/?id=3307. 10.07.2014].

Special attention should be paid to the carbon fibers, which are obtained by pyrolysis of the precursors. Such substrates are usually organic compounds, including polymers (the most common is polyacrylonitryle (PAN) or cellulose).

Fig. 13 shows schematically a process of pyrolysis of PAN, which is carried out initially in the presence of air and then under an atmosphere of nitrogen. Fig. 14 shows an image of a polymer composite containing carbon fibers, obtained by scanning electron microscopy (SEM).

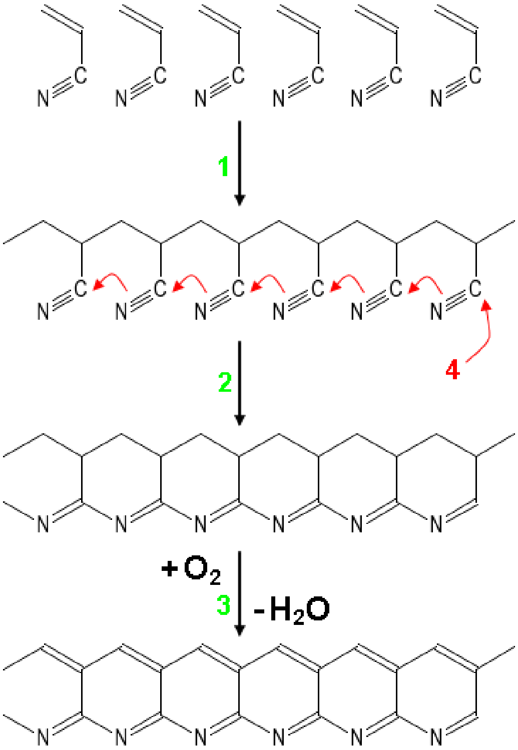


Fig. 13. Synthesis of carbon fiber from polyacrylonitrile (PAN): 1) Polymerization of acrylonitrile to PAN, 2) Cyclization during low temperature process, 3) High temperature oxidative treatment of carbonization (hydrogen is removed). After this, process of graphitization starts where nitrogen is removed and chains are joined into graphite planes [http://en.wikipedia.org/wiki/Carbon_%28fiber%29. 10.07.2014].

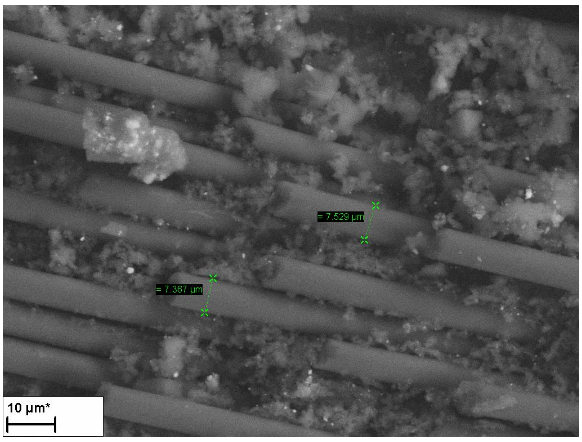


Fig. 14. SEM photo of the composite based on epoxy resin reinforced with carbon fibers, sample supplied by the Voith (German company), SEM made at Faculty of Chemistry, NCU.

In the first step, during oxidation, the ladder structure is formed; in the second - carbonization and proper orientation of the structure occurs. The final step at very high temperature (> 1000□C) result in the structure of graphite. Carbon fiber properties depend on conditions of the pyrolysis process. Polymer composites of carbon fibers are characterized by low density (hence, the products are light), antistatic properties, reduced flammability, low absorption of X-ray radiation, rigidity and very good mechanical properties.

Recently, the oriented polymer fibers (polyethylene - PE, polypropylene - PP, polyamide - PA, PET, poly (butyl terephthalate) - PBT) are often used to reinforce the composites structure. On the other hand, the vegetable fibers (cotton, jute, linen) provide a partial biodegradability of materials and leads to the higher water absorption and poor adhesion to hydrophobic polymers.

Currently, polymer composites found broad application in many sectors of the economy and industry, as well as in everyday life including (Fig. 15):

- automotive and transport (car bodies, parts of wagons),
- in the construction industry (structural elements, roofing, electrical insulating boards, helmets),
- in the aerospace, shipbuilding, aerospace,
- in the army and police (helmets, bulletproof vests),
- in electronics, electrical engineering and telecommunications,
- in paper industry (reinforced paper, book covers),
- in the production of household appliances, kitchen equipment, bathrooms accessories,
- in the packaging industry (including food, pharmaceuticals and cosmetics packaging),
- in the production of sports equipment (balls, hockey sticks, skis, tennis rackets, pole jumping, parts of footwear and clothing, knee pads and other protective accessories)
- in medicine (implants) and dentistry (dental fillings, dentures).

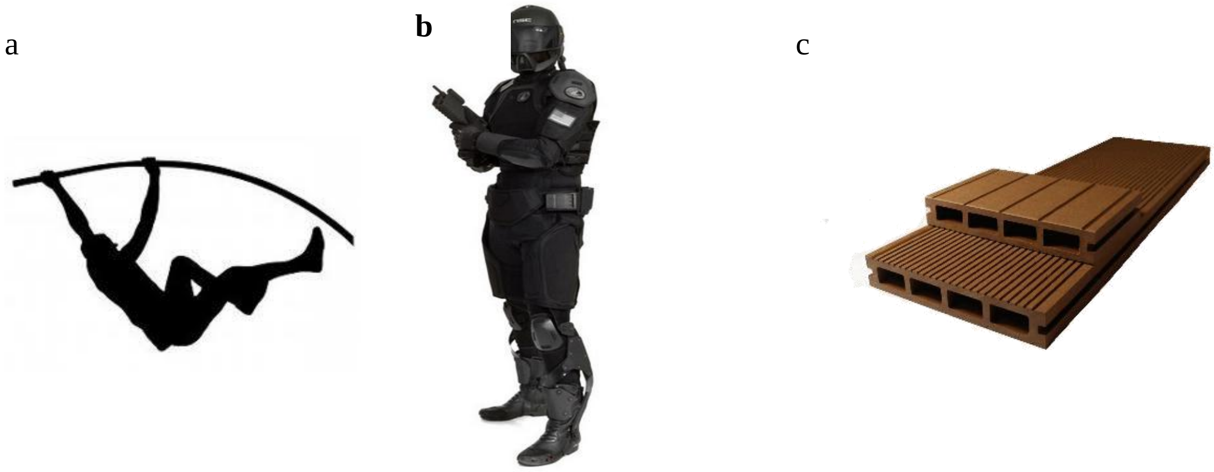


Fig. 15. Examples of application of polymer composites: a - in sports, b - in the military, c - in construction.

Polymer composites on an industrial scale are obtained by various methods:

- mixing of the components in the solid state – dry blend,
- mixing the components at a temperature above the glass transition temperature of the polymer (in the melt),
- reactive blending (co-extrusion, thermoforming, extrusion),
- blending of the components in a polymer solution and evaporating of the solvent.

In technological processes, the many types of equipment: drum mixers, conveyors, ball mills, rolling mills, crushers, and extruders are used for mixing.

Preparation of new composite materials for specific applications is usually preceded by a detailed study of the designed systems, allowing the optimization of the composition and conditions of their manufacturing.

Research on the properties of polymer composites are made according to its intended use by classic methods commonly used for conventional plastics. There are following studies:

- tensile strength, compressive strength, impact strength,
- rheological
- flammability test and resistance to high temperatures,
- the barrier properties
- optical and electrical properties.

In order to find the correlation between the structure of composites and their functional properties, advanced methods of instrumental analysis have to be applied to determine the chemical structure of the polymer and the modifier, degree of order (crystallinity) and type of intermolecular interactions determining adhesion. These methods include FTIR absorption spectroscopy, UV-VIS and Raman spectroscopy; X-ray diffraction (XRD), scanning electron microscopy (SEM, TEM), atomic force microscopy (AFM), thermogravimetry (TA), differential scanning calorimetry (DSC), elemental analysis, and others.

2. Nanomaterials and nanotechnologies

History of nanomaterials is quite long but rapid development of nanotechnology in recent decades has led to the production of modern materials with unique properties and versatile applications [11-20]. The significant contribution in nanotechnology progress had important scientific discoveries awarded the Nobel prizes, which include:

- Construction of microscopes with atomic resolution and development of scanning microscopy methods (scanning tunneling microscope - STM, atomic force microscopy - AFM and SEM and TEM).
- discovery and exploration of the properties of fullerenes
- discovery and characterization of carbon nanotubes and inorganic
- molecular beam methods and their application to the creation of quantum wells, quantum wires and quantum dots.
- the production of ultra-thin layers of crystal methods:
  a) metal organic chemical vapor deposition (MOCVD) - depositing a layer on the surface of materials through the use of organometallic compounds in gaseous form;
  b) molecular beam epitaxy (MBE) - technique involving the deposition of thin semiconductor layers, molecular (or atomic) beam in ultra-high vacuum ($p \leq 10^{-7}$ Pa); currently used in mobile telephones and wireless network communication (Wi-Fi).

3. Polymer nanocomposites

Polymer nanocomposites are a special type of composites - multicomponent systems manufactured in order to obtain special properties, better or completely new to those who have individual components. They consist of a polymer matrix and dispersed nanofillers or nanomodifiers i.e. substances of nanometric particle size (i.e. the order of 10^{-9}m) [21-40]. The term "nanocomposites" is often used to distinguish the materials from microcomposites in which the filler particles typically have a size greater than 100 nm, and macromolecules not have the ability to penetrate into their phase.

The first polymer nanocomposites have been described already in the 50s of the twentieth century. Polyamide nanocomposites were developed developed in 1976; in the 90's, Toyota began work on polymer composites with mineral fillers - layered aluminosilicates. Since then, fast increase in research on polymer nanocomposites and various nanofillers is observed. They are currently more often applied in many industrial branches. At the moment, the world production of polymer nanocomposites is about 1.5 thousand tons, of which one thousand tons are montmorillonite reinforced polyamides for the packaging and automotive industry. 0.5 thousand tons of carbon nanotubes reinforced nanocomposites based on poly (phenylene oxide) and polyamide are designed to the production of automotive parts.

It is estimated that the polymer nanocomposites market is worth approximately 211 million dollars, and over the past five years has increased by over 100 percent. Ford intends to implement dashboards and body panels made from new nanocomposites. The aim is to increase the scratch and surface damage resistance. The possibility of using the improved barrier properties of polymer nanocomposites in the construction of plastic fuel tanks is seriously examined.

Typically, at least one dimension of nanofiller - the diameter or thickness is in the range from several to 100 nm (it is assumed that the size should not exceed 500 nm). Depending on the amount of filler particle size occurring at the nanoscale, there are three groups of nanocomposites:

- Three dimensions in the nanoscale or the radius of the order of nanometers as in the case of spherical particles (silica or fullerenes);
- Two dimensions at the nanoscale and the third dimension greater - for example, nanofibers or carbon nanotubes;
- Only one dimension in the nanoscale, and the other higher - for example, phyllosilicates of nanometric thickness of the tile.

The small size of nanofillers in the polymer matrix significantly alters the material properties in comparison to microcomposites: the mechanical strength increases several times; the thermal conductivity decreases several times; microhardness increases (e.g. in the case of 10% by volume of n-Al_2O_3-SiC nanofiller twofold); moves the yield strength; abrasion resistance and barrier properties increases.

The most important benefits of the use of nanocomposites (in contrast to classical microcomposites) may include practically unchanged density of the material relative to the polymer matrix. This is possible since the polymer is usually added in not more than 5 wt% filler. Another preferred aspect is the ease of the material processing - a small addition of the filler does not affect the processing of the material. Polymer nanocomposites are processed all the techniques that are used for conventional plastics. The low price of some nanofillers such as montmorillonite (clay mineral often occurring in nature) is important. It makes the nanocomposites with MMT are also very cheap.

Since nanofillers may exist in different forms (grains, fibers, layers), hence different morphology of nanocomposites are possible, as schematically illustrated in Fig. 16.

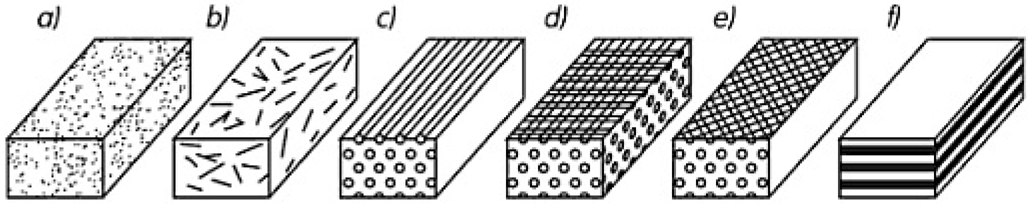


Fig. 16. Reinforced nanocomposite building models: a) particles, b) the short fibers, c) long fibers, d) grid, e) grids differently oriented in successive layers, f) laminated [Zawora J., Podstawy technologii maszyn, WSiP, Warszawa, 2013].

Nanocomposites properties depend on the type of filler and polymer, the size of the nanoparticles, the degree of dispersion as well as adhesion and intermolecular interactions between the components. The interplay is determined by the presence and reactivity of the functional groups capable of forming covalent, ionic or hydrogen bonds at the interface of the polymer-filler.

Polymer nanocomposites are typically obtained by the physical mixing of the polymer melt under shear and elevated temperature (during processing), in the polymer solution, or by *in situ* polymerization. The latter method consists in obtaining mixture of the monomer and the modifier, and then subjecting to polymerization process under suitable conditions.

The advantages of polymer nanocomposites are following:

- Large values of the modulus of elasticity,
- High impact strength,
- High deformability,
- Good performance for ultimate strength and fatigue
- Low density constructions providing savings vehicles,
- Good barrier properties with respect to gas permeation,
- High resistance to solvents,
- Optical transparency,
- Electrical conductivity,
- Increased fire resistance,
- Increased thermal resistance and stability,
- Good resistance to aging, corrosion, photodegradation,
- Polymeric nanocomposite products may have any shape and size, the elements are additionally very easy assembled,
- The possibility of obtaining nanocomposites involving biocidal silver nanoparticles.

Disadvantages of polymer nanocomposites:

- Manufacturing problems

a) Quite difficult manufacturing technology

b) Relatively difficult processing. Composites cannot be easily cut and drilled.

c) Composites cannot be welded; permanently joining elements is very difficult.

- Repair of devices based on nanocomposites

Repair of composite parts is substantially impossible contrary to the metal parts, which can be welded thanks to the plasticity of the metal and can be restored to their original shape.

- Ductility / brittleness - nanocomposites have little ductility and are usually brittle.
- High price

Applications of polymer nanocomposites:

- Construction materials
- Protective coatings
- Packaging materials
- Parts of machinery and bearings

- Engine parts
- Abrasives
- Biomedicine and dentistry (implants, dentures)

Polymer nanocomposites filled by layered fillers such as montmorillonite (MMT) have increasing practical importance. Researches allow for an exact knowledge of the structure of these type nanocomposites, which is schematically shown in Fig. 17. In the case of introduction of the layered filler into the polymer, two-phase system consisting of continuous matrix and domains of dispersed filler particles with unchanged structure can be formed (Fig. 8a). If the polymer molecules penetrate between the MMT plates, intercalated structure is obtained (Fig. 8b). In this case, the d-spacings increase (plates move away from each other), but a filler is still in the ordered (crystalline) form. The third possible structure (Fig. 8c) is the exfoliated (delaminated) nanocomposite in which MMT monolayer’s are completely separated from one another and arranged randomly in a polymer matrix. The structure of the system is completely amorphous.

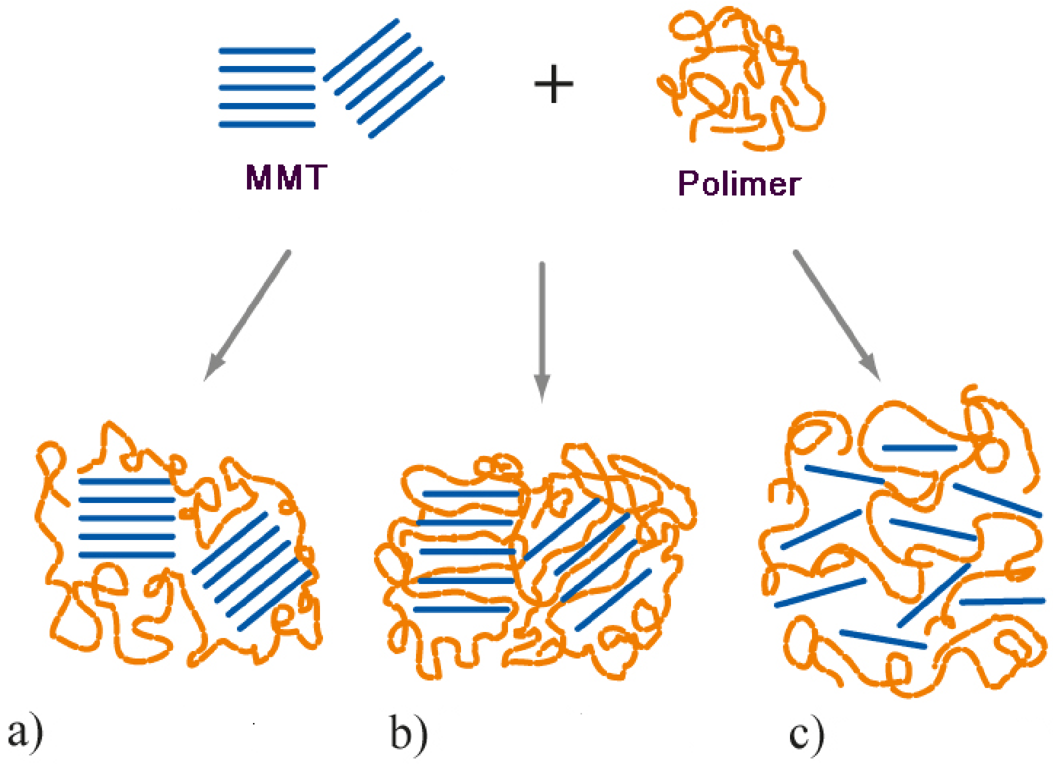


Fig. 17. Structure of polymer nanocomposite with montmorillonite: a) two distinct phases of microcomposite, b) intercalated nanocomposite, c) exfoliated nanocomposite [Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Materials Science & Engineering. 2000; 28(1-2):1-63].

The major application of the selected polymer nanocomposites with layered silicates (montmorillonite):

- Construction materials:
  Polymeric materials with high rigidity, chemical resistance and improved barrier properties.
  Matrices: polyamides, polyesters, polyolefins, polyacrylics
- The automotive industry:
  Outer body parts made of plastics, engine housing components.
  Matrices: polyamides, polypropylene
- Packaging industry
  Reinforced transparent PET bottles with a reduced permeability of gases (CO_2); packaging films with reduced permeability of gases (H_2O, O_2).
  Matrices: polyamides, polyesters
- Electrical and electronics
  Wire insulation flame-retardant. Housings of electronic devices.
  Matrices: blend of polyethylene and copolymer of ethylene and vinyl acetate (PE/EVA).

4. Nanofillers

The most commonly used nanofillers in modern polymer nanotechnology include:

- layered (lamellar) nanofillers - aluminosilicates such as montmorillonite, MMT),
- natural and synthetic nanofibers,
- the various allotropic forms of carbon: fullerenes, carbon nanotubes, graphite, and carbon black (amorphous carbon),
- inorganic nano-powders (calcium carbonate, aluminum oxide, zinc oxide, silicon nitride, hydroxyapatite, polyhedral silsesquioxanes),
- nanoparticles of metals and metal compounds (e.g. metal oxides), including noble metals.

Lamellar fillers are silicates which are caused by sharing of three oxygen atoms of the SiO_4 tetrahedron and adjacent tetrahedra, thus producing a two-dimensional infinite layer. Individual layers having a thickness of about 1 nm are interconnected by electrostatic interactions between metal ions, located in interlayer spaces, called galleries. For phyllosilicates belong clays and mica.

The most frequently used is montmorillonite described by formula $Na_{0,6}[(Mg_{0,6}Al_{3,4}) Si_8O_{20}(OH)_4]$ and kaolin $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The addition of these materials in the highly dispersed form (tiny powder) to polymers significantly improves the strength of plastic, increases its stiffness, flame-retardant, etc.

The selected nanoadditives and their influence on the properties of the polymer nanocomposite are listed below:

- Montmorillonite – good barrier properties (gas, odor, moisture, flame),
- Fullerenes, nanotubes – improvement of the mechanical and electrical properties and durability,
- Silica – improvement of the mechanical properties and heat resistance
- Metals and their compounds – increased electrical and thermal conductivity, catalytic activity, modification of the optical properties (for example, TiO_2 is a catalyst for many reactions e.g. photolysis of water, strongly scatters ultraviolet radiation while transmits visible light;
- Nanoparticles of noble metals (Ag, Cu) – antibacterial properties;
- Nanoparticles of iron compounds such as magnetite – superparamagnetic properties;
- Aluminum compounds – explosive (pyrophoric);
- Inorganic nanoparticles – modifiers of processing properties (increasing friction);
- Lubricants such as graphite and molecular lubricants (sulfides of tungsten and molybdenum) – reduction of friction, improvement of processing properties.

The nanoparticles are characterized by a high variability of the shape, size, chemical composition and stability, which mainly depend on the conditions of their preparation. Many research aims to develop methods to obtain repeatable systems with clearly defined geometry of nanoparticles, ensuring the stability of physical and chemical properties.

Nanofillers prices vary considerably, and therefore determine the final price of the nanocomposite. The most expensive include the carbon nanotubes and fullerenes.

5. Montmorillonite – structure, properties and modification

Montmorillonite (MMT) is a filler of high practical importance, and nanocomposites with its addition are the subject of many scientific papers. It is a component of natural minerals (clays), such as bentonite. MMT is composed of magnesium aluminosilicate. It consists of parallel layers (platelets), whose thickness is approximately 1 nm, and the dimensions of the surfaces are in the range 200 - 1000 nm. Between the plates, built with 2 outer layers of tetrahedrals and internal octahedral (Fig. 18), occur interactions leading to formation of agglomerates (packets), existing in polymer composites as separate domains. Silicate layer (SiO_4^{4-}) has a negative charge balanced by exchangeable cations Na^+, Ca^{2+}, and cations of the octahedral layer (Al^{3+} , Mg^{2+}, Fe^{3+}).

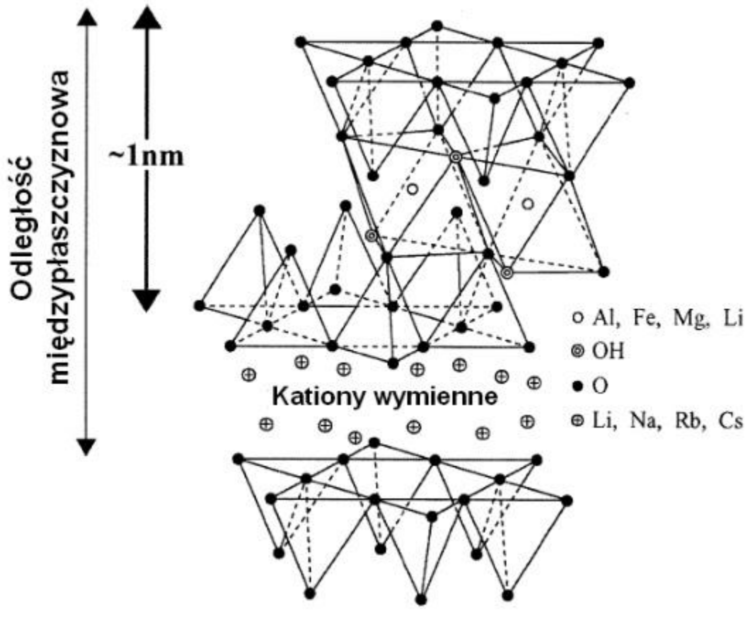


Fig. 18. The structure of montmorillonite (MMT) [Yu W., Zhao Z., Zheng W., Song Y., Li B., Long B., Jiang Q.: Structural characteristics of poly(vinylidene fluoride)/clay nanocomposites, Materials Letters, 4-5, 747-750, 2008].

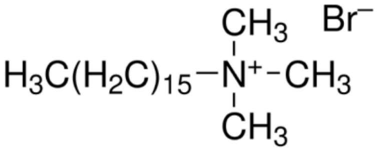
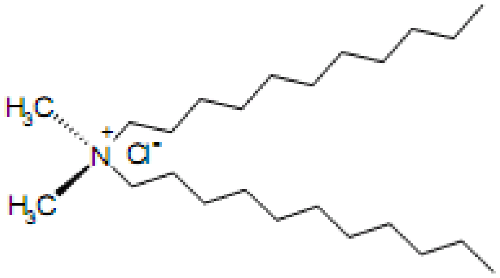
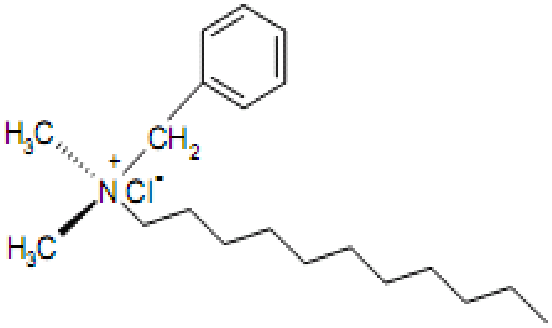
Montmorillonite surface is very high. Using 1g of nanofiller developed for individual lamellae could encircle the Earth. Due to the geometry of this mineral, also surface area of the polymer-filler interactions is very large.

A characteristic feature of MMT is the ability to internal exchange of cations, allowing its modification. MMT of natural origin is hydrophilic, making it difficult to mix with the hydrophobic polymers used in the manufacture of nanocomposites.

To tackle this problem, the MMT is subjected to surface modification (hydrophilization, organofilization) by means of suitable amphiphiles.

The modification consists in the introduction of aluminosilicate quaternary ammonium (aliphatic or aromatic) between the plane of the MMT, which leads to an increase in the distance between them and thus enables a penetration (intercalation) of the polymer or monomer.

Examples of the most commonly used of montmorillonite amine modifiers are given below:

Hexadecyltrimethyloammonium bromide (HTAB)	 $H_3C(H_2C)_{15}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3 \quad Br^-$
distearyldimethylammonium chloride (SMAC)	
stearylbenzyldimethylammonium chloride (SBMAC)	

The formation of the intercalated nanocomposites is possible when the spacings in MMT are comparable to the size of the macromolecules.

The process of organophilization of bentonite using hexadecyltrimethylammonium bromide (HTAB) and images of the nanocomposite in an organic solvent is shown in Fig. 19.

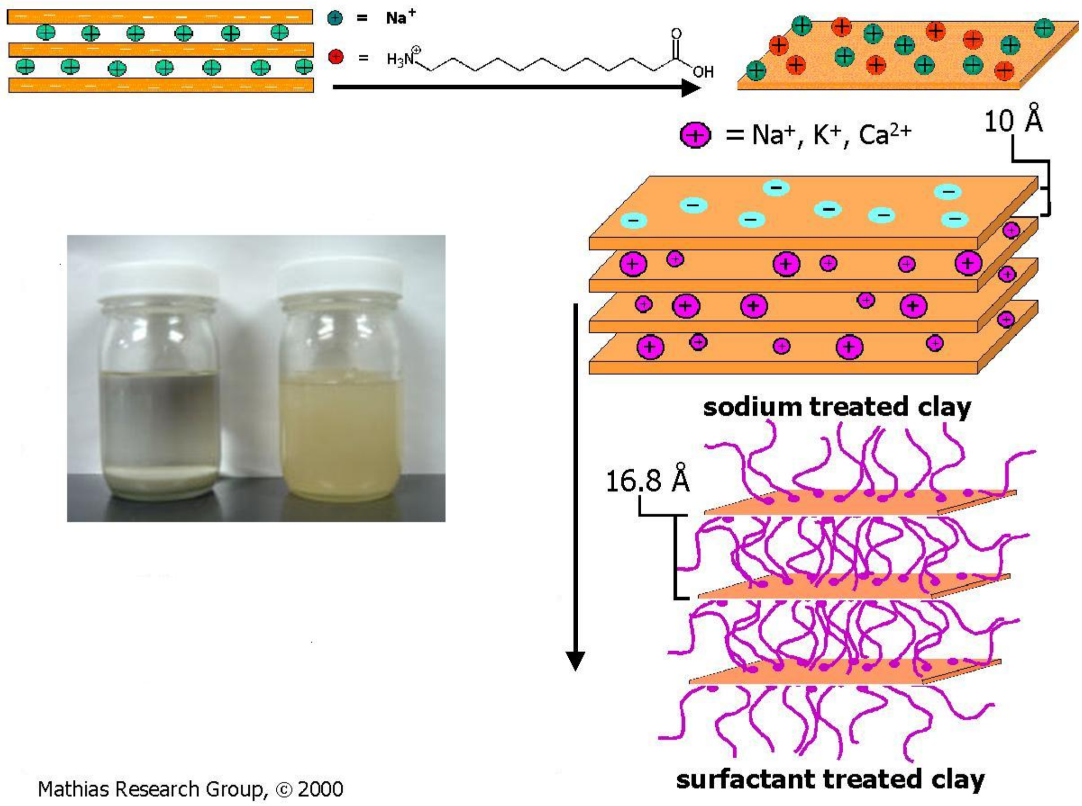


Fig. 19. Scheme of bentonite modification leading to increase of d-spacing http://chemsrv1.uwsp.edu/mathias/students/lsomlai/lsssum3.htm] and picture of dispersed in toluene clay before (left) and after modification (right) [http://www.kunimine.co.jp/english/bent/bent_01.htm].

Experimental evidences for the increase of distance between planes in MMT as a result of the modification provides X-ray diffraction (XRD). As can be seen from Fig. 20, the signal initially appearing at diffraction angle $2\Theta = 8°$, after modification occurs at approximately 4.5°. It means that d-spacing was changed from 1.244 nm to 2.044 nm.

The selection of the modifying agent enables the proper initial delamination of montmorillonite, which facilitates diffusion of the monomer or polymer to interlayer areas. Intercalation of the monomer to the gallery of MMT resulted in a further move apart the layers. The effect is greater, when the amphiphile molecules used to organofilization of material are longer.

Scheme of the preparation of polymer nanocomposite with montmorillonite by three most commonly used methods is shown in Fig. 21.

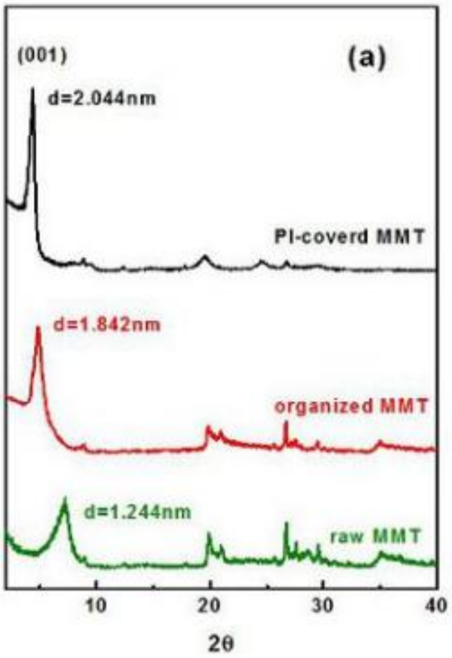


Fig. 20. XRD changes caused by modification of MMT structure and polyimide-MMT nanocomposite [Chang-An Wang, Huirong Le and Yong Huang (2010). Rapid Assembly Processes of Ordered Inorganic/Organic Nanocomposites, Biomimetics Learning from Nature, Amitava Mukherjee (Ed.), InTech,.: http://www.intechopen.com/books/biomimetics-learning-from-nature/rapid-assembly-processes-of-ordered-inorganic-organic-nanocomposites].

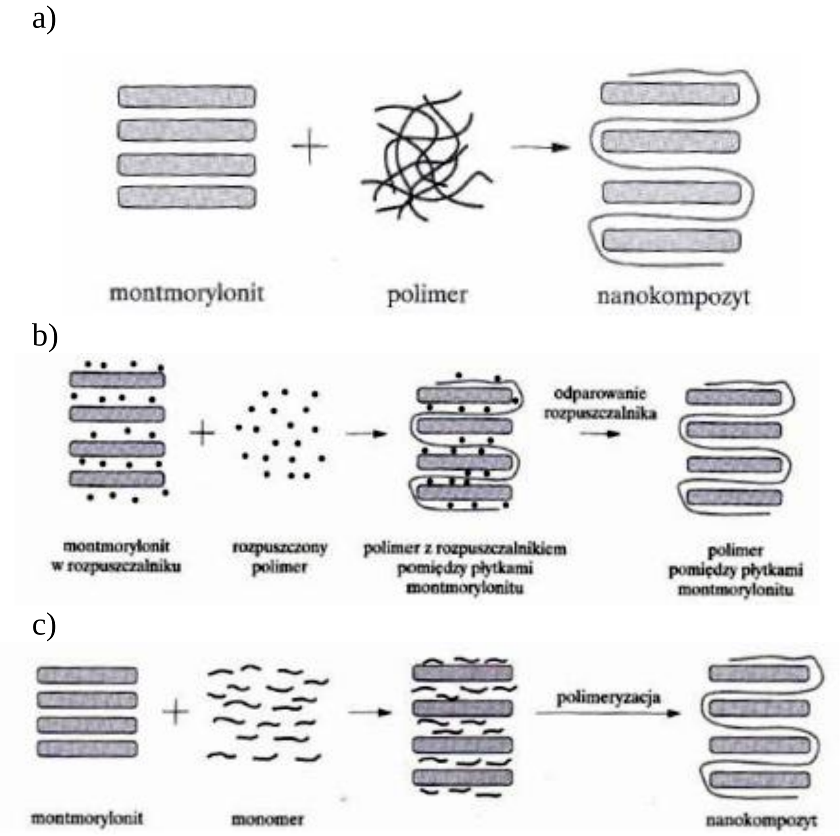


Fig. 21. Preparation of MMT-polymer nanocomposite by: a) polymer melt extrusion, b) a solvent method and c) polymerization *in situ* [Kurzydłowski K., Lewandowska M., "Nanomateriały inżynierskie konstrukcyjne i funkcjonalne", PWN, Warszawa, 2011].

In the case preparation of nanocomposites by mixing the ingredients under shear stress, the aluminosilicate layers undergo delamination due to the influence of mechanical forces. The decisive factor is the viscosity of the melt - the lower, the better the efficiency of the transfer of stress from the processing machine through the matrix to the particles of the mineral.

In situ polymerization method is mainly used in the preparation of thermoset polymer nanocomposites. In this case, synthesis consists of two stages:

- *First step* - involves penetration of liquid monomer between the plates of nanofiller; This initiates the process of separation of the silicate platelets, the duration of this step is dependent on the polarity of the monomers, the properties of nanofiller and the process temperature,
- *Second step* - the polymerization of the monomers is taking place in the spaces between the plates of the filler, which results in further increasing the distance between the silicate layers and can lead to total exfoliation of MMT.

Another type is the solvent method, which has been used in the preparation of nanocomposites with thermoplastics such as high density polyethylene – HDPE and polyamide - PA. It consists of three stages:

- *First step* - involves preparing a suspension of nanofiller in a polar solvent which will cause increase of the distance between the plates,
- *Second step* - at this stage, the polymer is dissolved in a polar solvent, the same that was used to prepare a suspension of the filler, followed by mixing of both components, i.e. the dissolved polymer and filler dispersion,
- T*hird, final step* includes solvent evaporation, drying and granulating of the resulting nanocomposite.

Delamination of MMT can be tested experimentally. It is helpful here, both X-ray diffraction (complete disappearance of the signal characteristic of amorphous materials, Fig. 22) and high-resolution transmission electron microscopy (HR-TEM), which allows to observe the changes in inosilicate order.

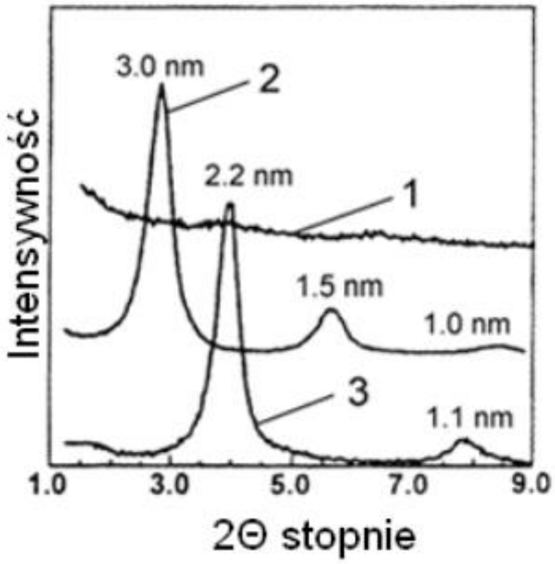


Fig. 22. X-ray diffraction of nanocomposites: 1 - exfoliated, 2 - intercalated, 3 - incompatible with the filler (microcomposite) [Królikowski W., Rosłaniec Z., "Nanokompozyty polimerowe", Kompozyty (Composites) 4, 2004, 3-16].

In order to obtain a stable nanocomposite, strong filler-matrix interactions should be induced. It allows overcoming the tendency to aggregation and therefore permanently separating aluminosilicate particles in the polymer matrix. The required thermal stability of the material obtained under processing conditions is achieved by using suitable surfactants.

An important feature of polymer nanocomposites is the improvement of barrier properties. This effect is used in the packaging industry. It can be explained by the difficult diffusion (and elongated path) of vapors and gases particles penetrating through nanocomposite film (Fig. 23).

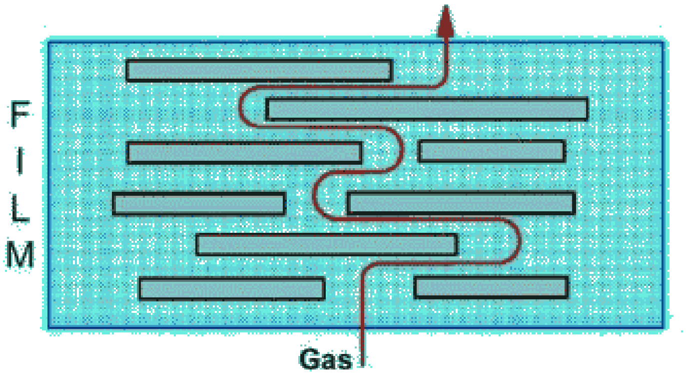


Fig. 23. Model of gas diffusion in nanocomposite containing platelet filler (the effect of the maze) [http://opakowania.com.pl/Wiadomości/Nanokompozyty-polimerowe-w-produkcji-opakowań-26099.html].

Accordingly modified MMT has been used successfully to form nanocomposites with polyolefins (polyethylene, polypropylene), poly(vinyl chloride), polyamides (nylons) or polystyrene.

6. Thermogravimetric analysis and determination of activation energy of nanocomposite decomposition

Thermal analysis in non-isothermal conditions is one of the methods for testing the thermal properties of the polymers. To this group belong derivatography measurements, i.e. coupled thermoravimetric analysis (TGA) and differential thermal analysis (DTA). Thermogravimetric analysis involves heating the sample at a constant rate and recording the temperature changes as a function of sample weight (TG curve) and the derivative of weight change (DTG curve). Differential thermal analysis involves heating the sample at a constant rate and measuring the temperature difference (i.e., the thermal effects of the difference) between the test sample and the reference substance (DTA curve). On the base of DTA curve, the glass transition temperature (T_g) and the melting temperature (T_m, in the case of semi-crystalline) polymers, as well as thermal effects (endothermic and exothermic) of physical processes and chemical reactions can be determined. Thermogravimetry is the most suitable method to study degradation processes of polymers [41] and it is used commonly for testing nanocomposites (Figs 24 and 24).

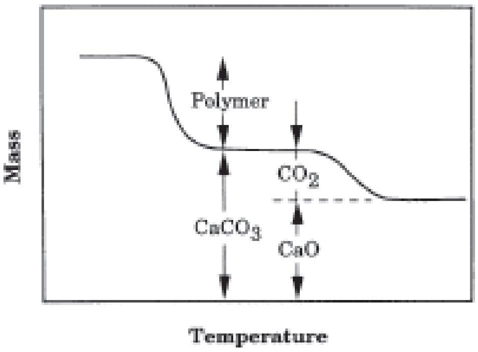


Fig. 24. An example of TG curve of polymer composite filed with $CaCO_3$ [U. W. Gedde, Polymer Physics, Thermal Analysis of Polymers, Springer, 1999].

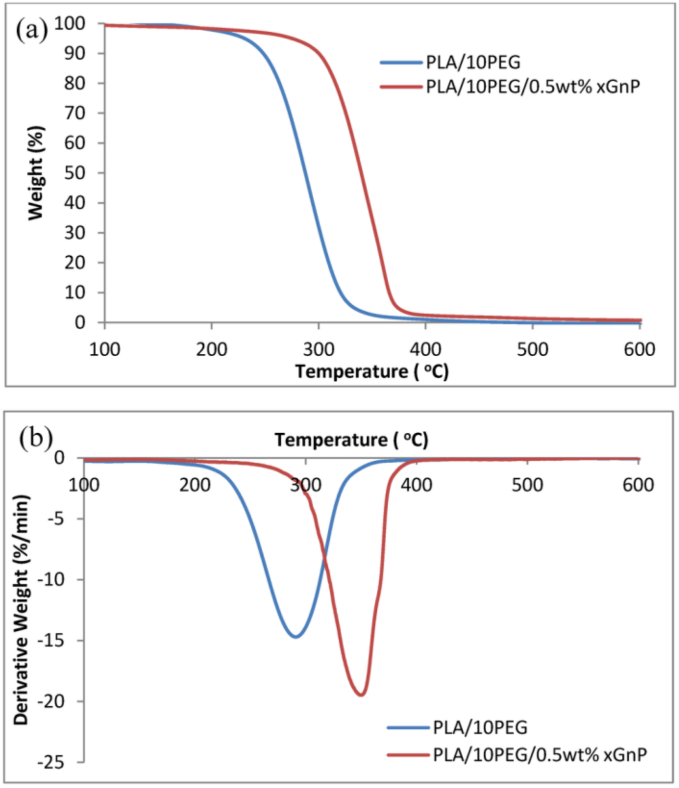


Fig. 25. Example of thermogravimetric curves (a - TG, b - DTG) of polymer blend (PLA / PEG) and a nanocomposite composed of the mixture and graphene filler; PLA - poly (lactic acid), PEG - poly (ethylene glycol) [B. W. Chieng , N. A. Ibrahim , W. M. Zin, W. Yunus, M. Z.Hussein, Poly(lactic acid)/Poly(ethylene glycol) Polymer Nanocomposites: Effects of Graphene Nanoplatelets, *Polymers* 2014, *6*(1), 93-104].

From recorded TG, DTG and DTA curves can be read the following parameters for determining of activation energy [41]:

- the temperature of decomposition onset, T_o, the point on TG curve, where the deviation from the initial constant value at zero conversion, α_o, is detected;
- the temperature at the maximum decomposition rate, T_{max}, corresponding to the minimum at the DTG curve;
- the temperature of the maximum rate of oxidation, T_{ox}, from the DTA curve peak (in the case of analysis in air or oxygen);
- the temperature of the decomposition end, T_k, at the final degree of conversion, α_k.
- weight loss (at any point of thermogravimetric curve), for example, initial (α_o) and a final degree of conversion (α_k).

Based on the derivatography measurements, apparent activation energy for thermal decomposition of the polymer can be determined [41, 42]. The basic equation of kinetic process of decomposition is:

$$\frac{d\alpha}{dt} = k * f(\alpha) \tag{1}$$

where: α - degree of conversion at a constant temperature based on the measured mass loss (from TG curve), i.e. $\alpha = [(m_o\text{-}m_t) / m_o] * 100\%$, m_o- the initial mass of the sample, m_t - mass after time t; k – reaction rate constant (rate constant of the nanocomposite thermal decomposition).

In the case of polymer degradation, it is assumed that the conversion ratio is dependent on the amount of undecomposed material according to the equation:

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

You can usually assume that the thermal degradation leading to gaseous products in the case of chain depolymerization reaction is first order (n = 1).

The dependence of the reaction rate constant (k) versus temperature is expressed by the Arrhenius equation:

$$k = A * \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where: E - activation energy, in this case, it is the apparent activation energy of the complex processes of polymer degradation, J/mol; R - gas constant, R = 8.314 J / (mol * K); T - absolute temperature, K; A - preexponential factor characterizing the frequency of acts of degradation.

Combining equations (1) ÷ (3) gives the basic relationship:

$$\frac{d\alpha}{dt} = A * (1-\alpha)^n * \exp\left(-\frac{E}{RT}\right) \tag{4}$$

For dynamic thermogravimetric analysis [43], the introduction of rate of heating, $\beta = dT/dt$, to equation (4) gives:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) * (1-\alpha)^n * \exp\left(-\frac{E}{RT}\right) \tag{5}$$

These equations were modified by various authors in order to determine the kinetic parameters of polymer degradation.

Methods for determining the apparent activation energy of the thermal decomposition of the polymers can be divided into two basic types:

- one-point method based on the maximum rate of degradation determined from TG and DTG curve. It is assumed that d (dα / dt) / dt = 0 if dα / dt = the maximum (Kissinger method).
- multipoint method for the entire range of conversion (whole TG curve), without any assumptions on α (Friedman, Flynn and Wall, Ozawa, Coats-Redfern and Horowitz-Metzger methods) [41].

6.1. Coats-Redfern method

Coats-Redfern equation [45-46], which represents a typical integral method can be represented by (6):

$$\int_0^\infty \frac{d\alpha}{(1-\alpha)^n} = \left(\frac{A}{\beta}\right) * \int_{T_1}^{T_2} \exp\left(-\frac{E}{RT}\right) dT \qquad (6)$$

For ease of calculation, the lower limit T_1 is usually taken as 0. After integration, this equation gives for n = 1:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) * \left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \qquad (7)$$

By plotting the left side of equation (7) from 1/T, activation energy (E) can be calculated from the slope

6.2. Horowitz-Metzger method

Horowitz and Metzger [47] simplified the exponential integral by particular approximation. They defined the characteristic temperature θ, such that $\theta = T - T_s$, where T_s is the reference temperature, in which $1-\alpha = 1/e$. Then, by making an approximation (8)

$$\frac{1}{T} = \frac{1}{T_s + \Theta} = \frac{1}{T_s\left(1 + \frac{\Theta}{T_s}\right)} \cong \frac{1}{T_s} - \frac{1}{T_s^2} \tag{8}$$

Finally, for *n* = 1, was obtained

$$\ln\ln(1-\alpha) \cong \frac{E\Theta}{RT_s^2} \tag{9}$$

The plot lnln(1-α) versus θ should give straight line with the slope *E/RT* ^{2}, from which
activation energy can be calculated.

6.3. Kissinger method

Kissinger method [48] refers to the maximum rate of degradation determined on the basis of TG and DTG. The relationship obtained by differentiating equation (4) is used. Taking into account the case where dα / dt = max, d (dα / dt) / dt = 0, i.e.

$$\frac{E*\beta}{R*T_{mr}^2} = A*n*(1-\alpha)_{mr}^{n-1} * \exp\left(-\frac{E}{RT_{mr}}\right) \tag{10}$$

where T_{mr} – temperature at maximum rate

Kissinger assumed that the expression $n*\left(1-\alpha_{\max}^{n-1}\right)$ is independent on □ and is equal to unity. Then after taking the logarithm, equation (11) is obtained:

$$\ln\frac{\beta}{T_{mr}^2} = \ln\frac{AR}{E} - \frac{E}{RT_{mr}} \tag{11}$$

From relation $\ln\frac{\beta}{T_{mr}^2}$ versus $1/T_{mr}$ apparent activation energy of polymer thermal decomposition can be calculated.

6.4. Ozawa method

Ozawa method [49] applies to the entire range of conversion (the TG curve) without additional assumptions about α. In this method, an approximation of Doyle is used [44, 50]. According to Ozawa, function F(α) is described by the equation:

$$\lg F(\alpha) = \lg\left(\frac{AR}{E}\right) - 2.315 - 0.4567 * \left(\frac{E}{RT}\right) \qquad (12)$$

This relationship is correct when $E/(R*T)>20$ and allows to calculate the apparent activation energy for any degree of conversion α. F(α) in the formula (12) is the integral of the function shown in equation (2). For the reaction described by first or pseudo-first order:

$$F(\alpha) = \ln\frac{1}{(1-\alpha)} \qquad (13)$$

then

$$\log\beta = \left[\log\frac{AR}{E} - 2.315 - \log F(\alpha)\right] - 0.4567\frac{E}{R}\left(\frac{1}{T}\right) \qquad (14)$$

Plottining $\log\beta$ versus $1/T$, a straight line can be obtained for a given degree of conversion, which is used to calculate the activation energy.

6.5. Friedman method

The most general differential method was developed by Friedman [44, 51, and 52], who used the equation (4) in the logarithmic form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \qquad (15)$$

(dα/dt) and T are determined for constant α and few heating rates β. The plot ln(dα/dt) versus $1/T$ has slope E/R and intercept point with coordinate axis $\ln[Af(\alpha)]$.

6.6. Flynn-Wall method

In the method of Flynn-Wall [44, 53], the equation (4) was modified to the form:

$$E = \left(-\frac{R}{b} \right) * \frac{d \ln \beta}{d \frac{1}{T}} \tag{16}$$

where: *b* – constant assuming that n = 1.

After the transformation

$$\log \left[\frac{\beta}{\left(1 - \frac{2RT}{E} \right)} \right] = \log \left[-\frac{AE_a}{Rf(\alpha)} \right] - 2.315 - 0.4567 \frac{E_a}{RT} \tag{17}$$

From the slope of a straight line on graph of log*β* versus 1/*T*, activation energy is calculated**.**

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Nanomaterials produced from the gas phase and polymeric nanocomposites

Laboratory

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Laboratory 1

The thin films prepared by Physical Vapor Deposition method

Dr Z. Łukasiak

Introduction

The thin films are very important in significant segments of engineering, microelectronics, chemical, nuclear and related industries but in our everyday life, too. The thin films are in sophisticated optoelectronic devices and in coating of simple sunglasses used. The thickness of deposits can vary from single monolayer of atoms to thick multilayers. The thin films can be by different techniques produced. The some of these techniques are simple and cheap, but can not assure control over thickness and structure of film produced. The most expensive and advanced is Molecular Beam Epitaxy (MBE) method. The MBE is in ultra high vacuum executed and assures full control over thickness of layer produced. The physical vapor deposition (PVD) method lie somewhere in the middle. The PVD is usually in vacuum performed but no ultra high vacuum regime is needed, apparatus is relatively simple and costs are not too high. The PVD method can be for production of virtually every type of inorganic materials - metals, alloys, compounds and mixtures, as well as some organic materials used.

Fundamentals of the Physical Vapor Deposition

The physical vapor deposition technology consist of the techniques of arc deposition, ion plating, sputtering, electron beam evaporation, resistance evaporation and many others. The Thermal Resistance Evaporation is simple one that can be used to produce full multilayer structure for organic light emitting diode (OLED), organic photovoltaic device (PVD) or organic field effect transistor (OFET). The scheme and principles of thermal resistance evaporation is shown on Fig. 1.

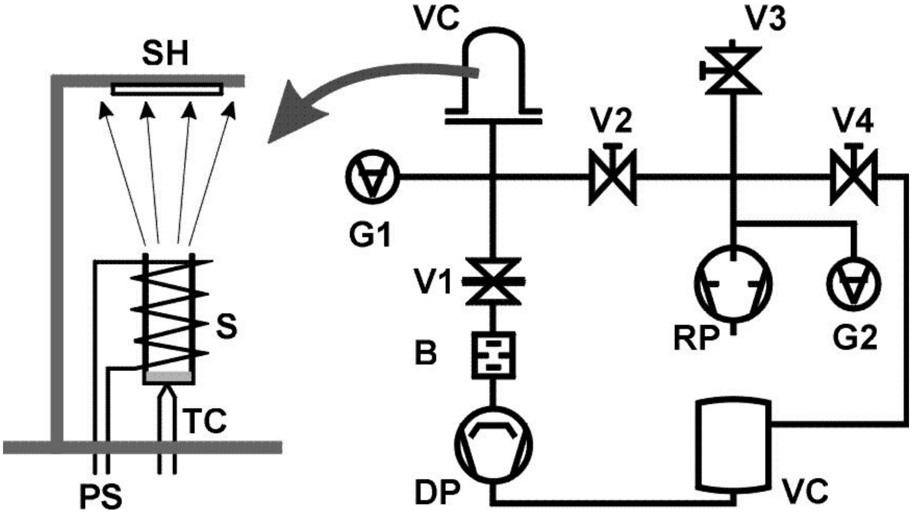


Fig. 1. Physical vapor deposition system designed for thermal resistance evaporation technique. Left part - evaporation equipment: S – source (crucible and heater), SH – sample (substrate) holder, TC – K-type thermocouple, PS – power supply (autotransformer). Right part – scheme of vacuum system: VC – vacuum chamber, V1-4 – manual valves, B – baffle, G1-2 – vacuum gauges, VC – equalization vacuum chamber, RP – sliding vane rotary vacuum pump, DP – diffusion pump

The principle of PVD process is simple. The substrates cleaned and prepared are in the main vacuum chamber to the holder attached. The holder is above evaporation source placed. As a evaporation source for metal films boat or wire heater can be used. For organic films (like small molecule compounds) usually quartz, glass or ceramic crucibles with resistive heaters are utilized. The thermocouple is touched do crucible for temperature monitoring. The temperature is changed by control of current from power supply applied to the heater. The high vacuum is produced by vacuum system consisting of vacuum pumps, gauges and valves. The more detailed explanations of vacuum system elements are in the next sections.

Basic terms and concepts in vacuum technology

Vacuum is defined in DIN Standard 28400-1 as the state of gas at which its pressure in vessel and therefore its particle density is lower than that of the ambient surrounding atmosphere or which the pressure of the gas is lower than 300 mbar, i.e. lower than the pressure of the atmosphere on the Earth’s surface [1].

Pressure is defined as the ratio as the ratio of force acting perpendicular and uniformly distributed per unit area.

$$p = \frac{F}{A} \qquad \text{(Eq. 3.1)}$$

where: p - pressure [Pa], F - force [N], A - area [m^2].

The unit for measuring pressure is the pascal. According to Eq. 3.1, the SI unit pascal is composed of Pa = N^*m^{-2}. The units mbar, torr and the units shown in Table 3.1 are common in practical use.

Table 1 - Conversion table for units of pressure.

unit	Pa	bar	torr	psi
Pa	1	$1*10^{-5}$	$7.5*10^{-3}$	$1.45*10^{-4}$
bar	$1*10^{5}$	1	750	14.5
torr	$1.33*10^{2}$	$1.33*10^{-3}$	1	$1.93*10^{-2}$
psi	$6.89*10^{3}$	$6.89*10^{-2}$	51.71	1

In practical use of PVD more important than pressure is mean free path. The mean free path is the average distance that a particle can travel between two successive collisions with other particles. For collisions of identical particles, the mean free path is described by:

$$\lambda = \frac{k \cdot T}{\sqrt{2} \cdot \pi \cdot p \cdot d_m^2} \qquad \text{(Eq. 3.2)}$$

where λ - mean free path [m], d_m - molecular diameter [m], k - Boltzmann constant, T - temperature [K]. From Eq. 3.2 it can be seen that the mean free path exhibit linear proportionality to the temperature and inverse proportionality to the pressure and molecular diameter.

In the vacuum technology vacuum is divided by convention in the few types for the selected pressure ranges, mean free paths and densities. Types of vacuum are in Table 2.

Table 2 - Pressure ranges in vacuum technology [2]

pressure range	pressure [Pa]	number density [cm^{-3}]	mean free path [m]
Atmospheric pressure	101.325	$2.7*10^{19}$	$6.8*10^{-8}$
Low vacuum (LV)	30000...100	$10^{19}...10^{16}$	$10^{-8}...10^{-4}$
Medium vacuum (MV)	$100...10^{-1}$	$10^{16}...10^{13}$	$10^{-4}...10^{-1}$
High vacuum (HV)	$10^{-1}...10^{-5}$	$10^{13}...10^{9}$	$10^{-1}...10^{3}$
Ultra-high vacuum (UHV)	$10^{-5}...10^{-10}$	$10^{9}...10^{4}$	$10^{3}...10^{8}$
Extremely high vacuum (XHV)	$< 10^{-10}$	$< 10^{4}$	$> 10^{8}$

For PVD important are high vacuum subrange and subranges from atmospheric pressure to medium vacuum called rough vacuum (RV).

Generation of vacuum

1. Classification of vacuum pumps.

Vacuum pumps are used to reduce the gas pressure in a certain volume and thus the gas density. Consequently consider the gas particles need to be removed from the volume. Basically differentiation is made between two classes of vacuum pumps [2]:

- pumps where, via one or several compression stages, the gas particles are removed from the volume which is to be pumped and ejected into the atmosphere (compression pumps). The gas particles are pumped by means of displacement or pulse transfer.
- pumps where the gas particles which are to be removed condense on or are bonded by other means (e.g. chemically) to a solid surface, which often is part of the boundary forming volume itself.

A classification which is more in line with the state-of-the-art and practical applications makes a difference between the following types of pumps, of which the first three classes belong to the compression pumps and where the two remaining classes belong to the condensation and getter pumps [2]:

- Pumps which operate with periodically increasing and decreasing pump chamber volumes (rotary vane and rotary plunger pumps; also trochoid pumps)
- Pumps which transport quantities of gas from the low pressure side to the high pressure side without changing the volume of the pumping chamber (Roots pumps, turbomolecular pumps)
- Pumps where the pumping effect is based mainly on the diffusion of gases into a gas-free high speed vapor jet (vapor pumps)
- Pumps which pump vapors by means of condensation (condensers) and pumps which pump permanent gases by way of condensation at very low temperatures (cryopumps)
- Pumps which bond or incorporate gases by adsorption or absorption to surfaces which are substantially free of gases (sorption pumps).

In the physical vapor deposition system shown on Fig. 1 rotary vane pump for rough vacuum and diffusion pump for high vacuum are used.

2. PVD system - rough vacuum pump

The rotary vane vacuum pump is an oil-sealed rotary displacement pump. The pump consists of a stator, an eccentrically placed rotor, vanes that move radially under centrifugal and resilient forces and the inlet and outlet. The eccentric placement of rotor and vanes divide the working chamber into two separate compartments with variable volumes. As the rotor turns, gas flows into the enlarging suction chamber until it is sealed off by the second vane. The enclosed gas is then compressed until the outlet valve opens against atmospheric pressure. The outlet valve is oil-sealed.

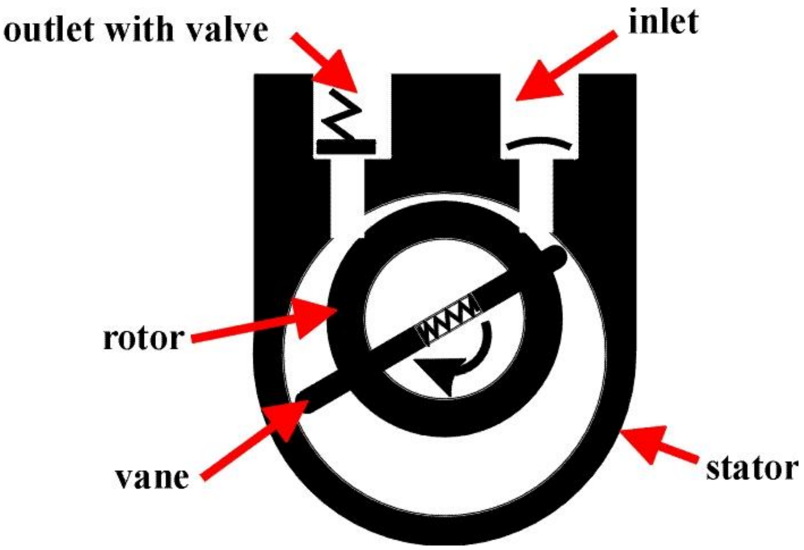


Fig. 2. The diagram of rotary vane vacuum pump [3].

Pump oil, which is also referred to as operating fluid, has multiple tasks to perform in a rotary vane pump. It lubricates all moving parts, fills both the dead volume under the outlet valve as well as the narrow gap between the inlet and outlet. It compresses the gap between the vanes and the working chamber and additionally ensures an optimal temperature balance through heat transfer.

3. PVD system - high vacuum pump

The oil diffusion pump is as a high vacuum pump in PVD system used. Diffusion pumps use a high speed jet of vapor to direct gas molecules in the pump throat down into the bottom of the pump and out the exhaust. These pumps consist basically of a pump body with a cooled wall and a three- or four-stage nozzle system. The oil serving as pump fluid is in the boiler and is vaporized from here by electrical heating. The pump fluid vapor streams through the riser tubes and emerges with supersonic speed from the ring-shaped nozzles. Thereafter the jet so-formed widens like an umbrella and reaches the wall where condensation of the pump fluid occurs. The liquid condensate flows downward as a thin film along the wall and finally returns into the boiler. Because of this spreading of the jet, the vapor density is relatively low. The diffusion of air or any pumped gases (or vapors) into the jet is so rapid that despite its high velocity the jet becomes virtually completely saturated with the pumped medium.

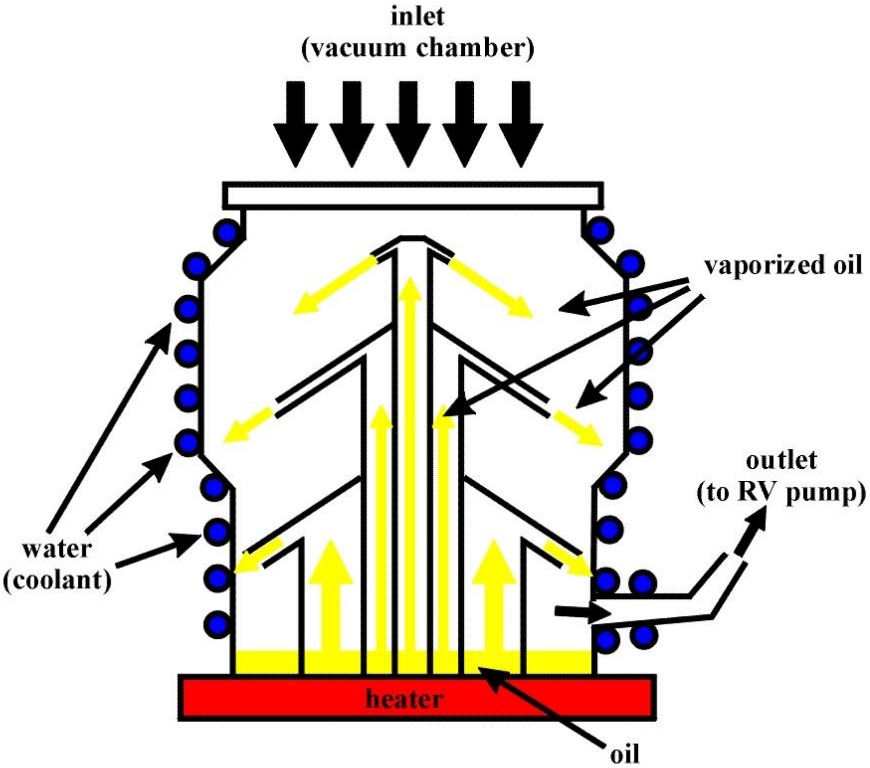


Fig. 3. The diagram of oil diffusion vacuum pump [3].

The basic diagram of operation of the oil diffusion vacuum pump is shown on figure 4.3.1.

WARNINGS!

The diffusion pump is very hot!

The diffusion pump always must be under rough vacuum before turning on!

The diffusion pump must be cooled by water during operation and at least 20 minutes after turning off!

The diffusion pump must be cool before venting with the air under atmospheric pressure!

Vacuum measurement

1. Introduction to vacuum measurement

The pressures measured in vacuum technology today cover a range from 1013 mbar to 10^{-12} mbar, i.e. over 15 orders of magnitude. Measuring instruments designated as vacuum gauges are used for measurement in this broad pressure range. Since it is impossible for physical reasons to build a vacuum gauge which can carry out quantitative measurements in the entire vacuum range, a series of vacuum gauges is available, each of which has a characteristic measuring range that usually extends over several orders of magnitude. In order to be able to allocate the largest possible measuring ranges to the individual types of vacuum gauges, one accepts the fact that the measurement uncertainty rises very rapidly, by up to 100% in some cases, at the upper and lower range limits. In PVD system from Fig. 2.1 two type of vacuum gauges are mounted: two thermal transfer gauge for rough vacuum (one on the inlet of rotary pump and second one in the vacuum chamber) and one cold cathode ionization vacuum gauge in the vacuum chamber for high vacuum measurements.

2. Pirani rough vacuum gauges

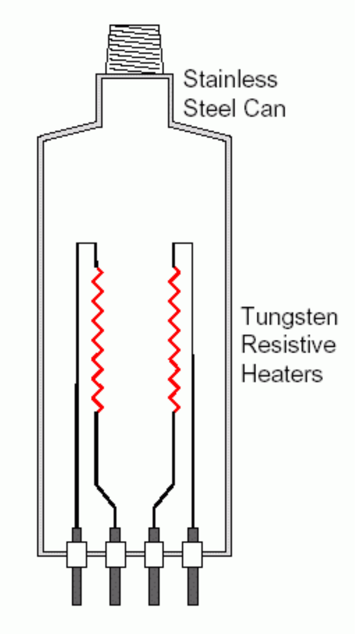


Fig. 4. The thermal transfer vacuum Pirani gauge

A Pirani (thermal transfer) vacuum gauge (Fig. 4.) utilizes the thermal conductivity of gases at pressures p of less than approx. 10^{-4} Pa to 100 hPa. Wire (usually tungsten) that is tensioned concentrically within a tube is electrically heated to a constant temperature between 110°C and 130°C by passing a current through the wire. The surrounding gas dissipates the heat to the wall of the tube. In the molecular flow range, the thermal transfer is proportional to the molecular number density and thus to the pressure. If the temperature of the wire is kept constant, its heat output will be a function of pressure. However it will not be a linear function of pressure, as thermal conductivity via the suspension of the wire and thermal radiation will also influence the heat output. This way measurement of voltage and current (power) applied to the wire gives the information about pressure.

3. Cold cathode ionization vacuum gauges (high vacuum gauges)

Cold cathode ionization vacuum gauges essentially consist of only two electrodes, a cathode and an anode, between which a high voltage is applied via a series resistor. Negatively charged electrons leave the cathode through field emission, moving at high velocity from the cathode toward the anode. As they travel this path, they ionize neutral gas molecules, which ignites a gas discharge. The measured gas discharge current is a parameter for pressure. However only few molecules are ionized in the case of straight electron trajectories, which results in lower sensitivity. To improve ionization efficiency magnetic field is used. A metal pin (anode) is surrounded by a rotationally symmetrical measurement chamber (cathode). An axially magnetized cylindrical, permanent-magnet ring is placed on the exterior of the measurement chamber to generate a magnetic field within the chamber. The electrons travel through the magnetic field on spiral trajectories. The electron paths extended in this manner increase the probability of collisions with the gas molecules and ensure that sufficient ions are generated to maintain the gas discharge.

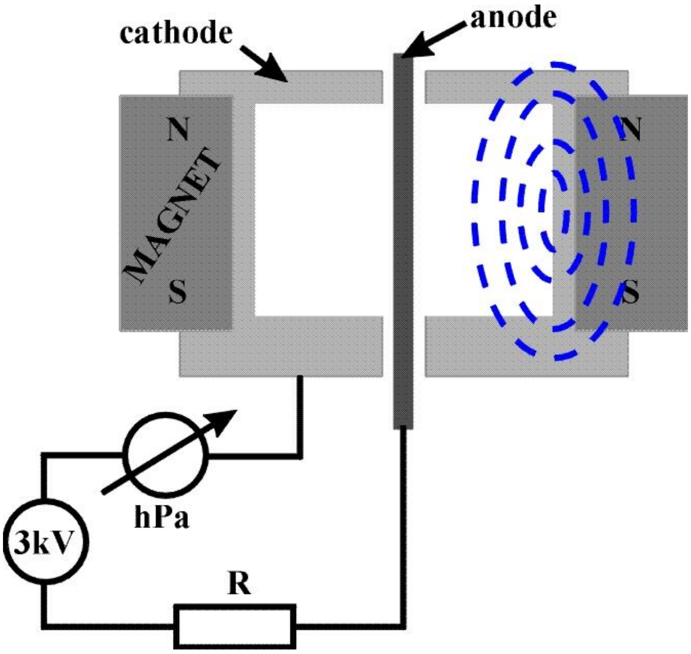
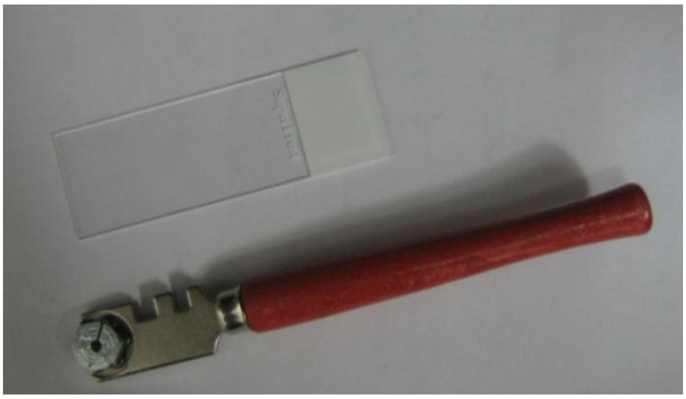


Fig. 5. The cold cathode ionization vacuum gauge.

Preparing of thin films using PVD method

1. Cleaning of substrates



As a substrates for thin films microscopic glasses are used. The glass have to be cut for small pieces using glass cutter. The final substrates typically are 9mm x 25 mm (dimensions result from dimensions of cleaning basket and sample holders in the vacuum chamber).

Fig. 6. The microscopic glass (substrate) and glass cutter.

The glass substrates must be cleaned before film deposition. The fallowing steps leads to clean substrates:

- immerse in mixture of detergent and deionized water (1:5) for 10 min. in the ultrasonic bath
- immerse in the deionized water for 3 min. in the ultrasonic bath
- immerse in the acetone for 15 min. in the ultrasonic bath
- immerse in the ethanol for 15 min. in the ultrasonic bath

WARNINGS!
DO NOT TOUCH SUBSTRATES!

USE TWEEZERS!

2. Preparation of depositing process

Depending of the type of films (metal or organic) masks or holders are used for keep substrates in the vacuum chamber.

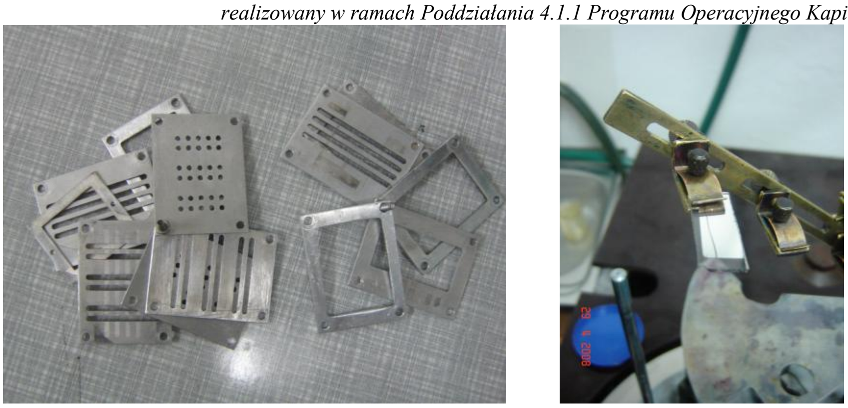


Fig. 7. The masks (left) for metal films and holder (right) for organic films in PVD system.

For the metal depositing tungsten heater and for organic material glass/quartz crucible are used.

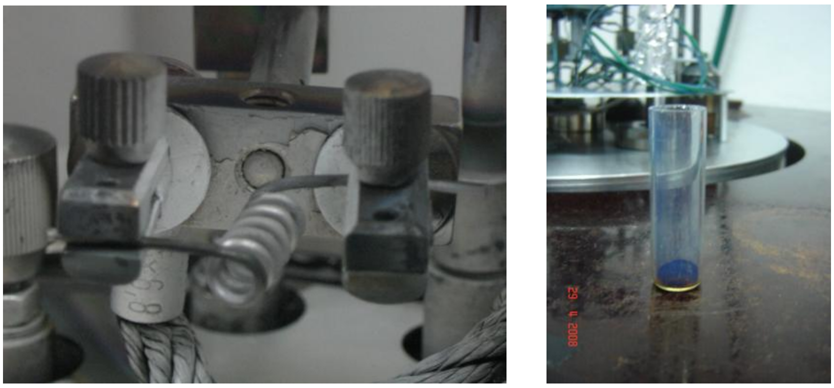


Fig. 8. The tungsten heater (left) for metal films and crucible (right) for organic films in PVD system.

3. Preparation of vacuum system

If substrates and depositing materials are ready, vacuum chamber (bell jar) can be closed. Before placing the bell jar in the PVD system its edges should be lubricated with vacuum grease to ensure tightness.

Fig. 9. The high vacuum grease (left), applying grease to the edges of bell jar (right).

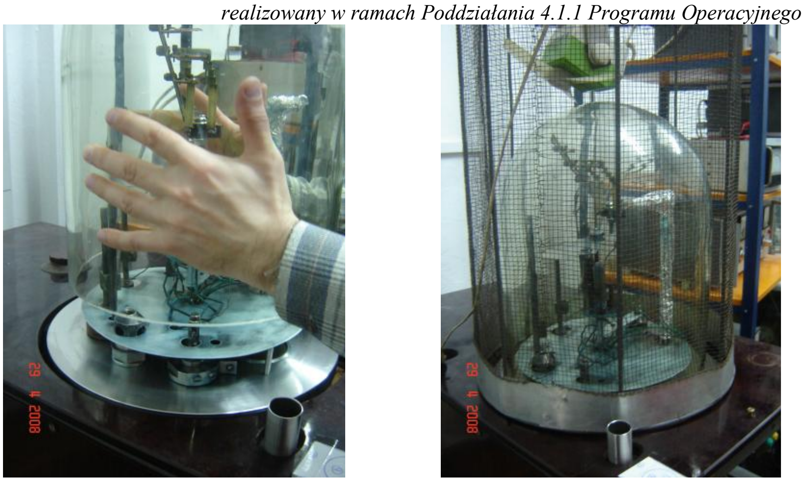


Fig. 10. Placing the bell jar (left) and metal net cover (right).

WARNING!

BELL JAR IS EXTREMALLY SENSITIVE TO THE IMPACT!

BE CAREFUL AND ALWAYS USE COVER DURING OPERATION!

Next step is preparing vacuum in the PVD system.

4. Pumping of vacuum system

The procedure of pumping occurs in the fallowing steps:

1. All valves are closed
2. Turn on rotary pump RP and rough gauge G2, wait 3 min.
3. Open the valve V2 to pump the main vacuum chamber VC. After 20-30 min pressure in VC have to be approx. 10^{-2} Torr.
4. Close the valve V2, open valve V4, open cooling water and next turn on diffusion pump DP, wait 30 min until the DP is fully hot.
5. Test pressure in main vacuum chamber. If necessary close V4, open V2 for 2-3 min. Return to position described in point 4. (V2 close, V4 open)
6. Open V1, turn on high vacuum gauge G1.
7. Wait approx. 60-90 min. to get high vacuum (approx. 10^{-5} Torr)
8. System is ready to deposit the film.

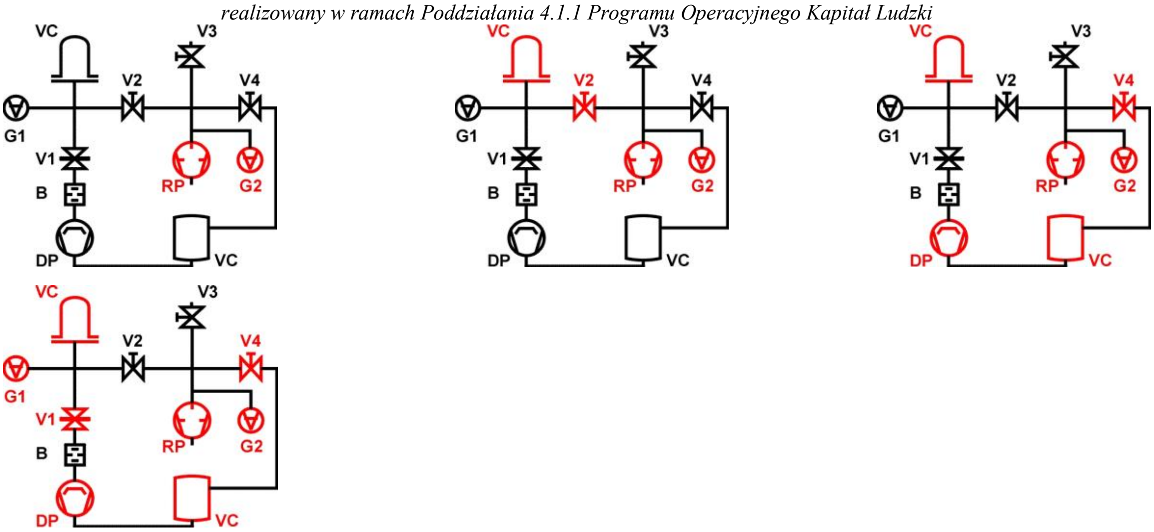


Fig. 11. The steps of pumping of PVD system.

5. Depositing of the film

WARNING!
DURING EVAPORATION TURN OFF ALL GAUGES!

Example 1. Aluminium

1. Turn on the power supply
2. Set current from 10A to 40 A in 5 A steps. Wait 30s before each step
3. Look on the heater and increase current until Al start evaporation (after approx. 10 s all material is evaporated)
4. Set current to 0 in 10 A steps. Wait 10 s after each step.
5. Turn off the power supply.
6. Go to description of the procedure of venting.

Example 2. Organic layer - phtalocyanines

1. Turn on the power supply
2. Turn on the thermometer
3. Set current to approx. 10 A and wait until temperature reaches 150°C. Current will decrease during heating of crucible due to increasing the resistance of heater with temperature.
4. Increase current (near 10A) ant look on the thermometer
5. Phtalocyanines (CuPC, CoPc, MgPc, ZnPc) evaporate in 350-360°C

6. Venting of the system.

After deposition PVD system must be cooled and vented before open of the chamber.

The procedure of pumping occurs in the fallowing steps:

1. Close valve V1 and turn off the diffusion pump.
2. Wait until temperature of crucible reaches 50°C (approx. 30 min.)
3. Close valve V4, turn off rotary pump and open valve V3 - sound of hiss of air must be heard.
4. Open the valve V2- sound of hiss of air must be heard, too. Wait until chamber is fully vented. Wait 10 min.
5. Take off the bell jar, turn off the cooling water.
6. Take off the substrates.
7. Clean the parts of the system with ethanol.

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Laboratory 2

Synthesis, structural characterization, and studies of thermal properties of silver precursors used in chemical vapor deposition methods (CVD)

Dr A. Radtke

Review of the literature indicates that in the CVD methods as precursors are used compounds: inorganic, organometallic and silver(I) combination with organic ligands. Among the silver halide is used AgF, which allows for deposition of silver layer on silicic substrates, at a temperature of 873 K.

The most frequently used precursors in the CVD methods are β-diketonates of Ag(I) and their connections with the Lewis bases ([Ag(β-diketonate)(L)], L= PMe_3, PEt_3, VTES, BTMSA, BTMSE). Complexes [Ag(β-diketonate)(L)] are characterized by relatively low volatility, but higher stability. This is result of stronger interaction of Ag(I) atoms with the π-donor ligands, compared to analogous connections such as Cu(I). Deposition temperatures of complexes [Ag(hfac)(L)] (L = PMe_3, PEt_3, VTES, BTMSA, BTMSE) change in series: BTMSE<BTMSA<VTES<PEt_3<PMe_3.

Thermal stability of this type complexes with trimetylofosphane or trietylofosphane be based on the stabilization of Ag(I) coordination sphere with the use of σ-donor and the π-acceptor ligand properties. In the case of VTES, BTMS, BTMS ligands their σ-donor properties cause the weaker stabilization effects of Ag-O bond, which is reflected in lower deposition temperatures.

The objectives of exercise:
- understanding of the chemistry of the silver (I) precursors used in chemical vapor deposition method
- conducting controlled synthesis of precursors: $AgOOCC_2F_5$ and $[Ag(OOCCH_2{}^tBu)(Pet)_3]$
- carrying out spectroscopic characteristics of the silver(I) precursors (MIR, ^1H, ^{13}C NMR)
- Analysis of the thermal properties of silver(I) precursors

Reagents:

- $AgNO_3$
- C_2F_5COOH
- PMe_3, PEt_3
- Ar

Apparatus:

- Laboratory glassware (beakers, weighing vessels, round-bottom flasks)
- Magnetic stirrer and stirrer cube
- Vacuum Schlenk line
- CVD reactor

Exercise performance:

1. Synthesis of *$Ag(OOCC_2F_5)$*

$$2AgNO_3 + 2NaHCO_3 \rightarrow Ag_2CO_3\downarrow + 2Na^+ + NO_3^- + CO_2\uparrow + H_2O$$

$$Ag_2CO_3 + 2C_2F_5COOH \rightarrow 2C_2F_5COOAg + CO_2\uparrow + H_2O$$

I step: synthesis of silver carbonate

- Dissolve 29 g (0.17 mol) of $AgNO_3$ in 340 cm^3 of water and 30 g (0.36 mol) $NaHCO_3$ w150 cm^3 of water, and then mix together the solutions using a magnetic stirrer.
- A yellow-white precipitate Ag_2CO_3 should precipitate, which should be mixed for a further 10 minutes.
- Sludge drain and rinse several times with distilled water.
- Weigh the product after drying.

II step: synthesis of pentafluoropropionatosilver (I)

- Dissolve 10 g Ag_2CO_3 (0.036 mol) in 16 cm^3 of water, and then add 6.2 cm^3 of C_2F_5COOH.
- Keep the reaction in a round bottom flask with a magnetic stirrer at room temperature for 24 h.
- Drain and rinse the precipitate formed anhydrous alcohol.
- Transfer the filtrate to a crystallizer wrapped in black paper and leave to crystallize.

The crystallized compound should be analyzed using:

- Single crystal X-ray diffraction
- X-ray powder diffraction
- A spectroscopic analysis in the range of MIR
- Analysis of the 1H and 13C NMR
- Thermal analysis

2. Synthesis of *[Ag(OOCCH$_2$^{t}Bu)(PEt$_3$)]*

$$KHCO_3 + {}^tBuCH_2COOH \rightarrow {}^tBuCH_2COOK + CO_2\uparrow + H_2O$$

$$AgNO_3 + {}^tBuCH_2COOK \rightarrow {}^tBuCH_2COOAg + K^+ + NO_3^-$$

$${}^tBuCH_2COOAg + PEt_3 \xrightarrow{EtOH} [(AgCOOCH_2{}^tBu)(PEt_3)]$$

I step - synthesis of ^{t}BuCH$_2$COOK

- Dissolve 5.10 g (0.51 mol) of $KHCO_3$ in 100 cm^3 of water, and then add a solution of 3,3-dimethylbutanoic acid CH$_2$^{t}BuCOOH (5.79 g in 100 cm^3 of water).
- Stir the reaction mixture for one hour on a magnetic stirrer while maintaining a temperature of about 100^{o}C.
- After cooling to room temperature, the mixture should turn into colorless gel.
- Dry the resulting gel in a vacuum desiccator for 24 hours to obtain a white powder

II step - synthesis of ^{t}BuCH$_2$COOAg

- Dissolve 8.50 g (0.05 mol) of $AgNO_3$ in 20 cm^3 of water, and then add a solution of ^{t}BuCH$_2$COOK (7.83 g (0.05 mol) in 50 cm^3 of water)
- Stir the reaction mixture for 30 minutes on a magnetic stirrer and then the filtrate.
- Drained sludge should be dried in a vacuum desiccator over P_2O_5 for several days.

III step - synthesis of (AgOOCCH$_2$^{t}Bu)(PEt$_3$)

- Synthesis must be carried out in Schlenk flask, in the presence of argon.
- To a solution of silver(I) carboxylate ^{t}BuCH$_2$COOAg (2.24 g - 10 mmol, in 80 cm^3 of anhydrous ethyl alcohol) add 10 cm^3 of 1M solution PEt$_3$ (10 mmol) in THF.
- The reaction mixture should be stirred for 10 hours, in argon atmosphere.
- Precipitate should be filtered off under reduced pressure using a sheet G4.
- The filtrate should be concentrated under reduced pressure (5 mmHg).
- A product in the form of greenish-yellow oily liquid should remain in a Schlenk vessel, turned by black paper; it should be stored in the refrigerator.

The resulting compound should be surrendered by:

- Single crystal X-ray diffraction
- X-ray powder diffraction
- A spectroscopic analysis in the range of MIR
- Analysis of the 1H and 13C NMR
- Thermal analysis

The report of the exercise:

- Write the equation of chemical reactions in the synthesis of precursors of silver (I)
- Calculate yield of conducted syntheses
- Discuss the structure of a compound based on crystallographic data
- Make the analysis of IR and NMR spectra
- Review the results of the thermal analysis

Laboratory 3/4

Chemical vapor deposition of metallic silver layers from synthesized Ag(I) precursor and characteristic of structural and morphological properties of produced nanolayers

Dr A. Radtke

The objectives of the exercise:

- Familiarization with the construction of the CVD hot-wall reactor,
- Conducting chemical vapor deposition process from the vapor phase to form the silver layer,
- Morphological and structural analysis of silver layer, using X-ray film powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Apparatus:

- Hot-wall CVD reactor
- Powder diffractometer
- Scanning electron microscope
- Transmission electron microscope
- Ultrasonic bath

Reagents:

- Ag CVD precursor– $AgOOCC_2F_5$ (1)
- Ag CVD precursor– $[(AgOOCCH_2{}^tBu)(PEt_3)]$ (2)
- Ar

Exercise performance:

- The deposition process should be carried out in the presence of exercise assistant,
- Before the deposition process, prepare the substrate, degrease it and activate,
- Degreasing process:
  a) washing in acetone in ultrasound bath for 15 minutes at room temperature, drying air flow;

b) re-washing by ultrasonic scrubbing with 99.8% ethanol for 15 minutes at room temperature, washing the substrate in distilled water;

c) washing in a subsequent ultrasound bath with distilled water for 15 minutes at room temperature;

d) drying in the stream of inert gas (argon).

- The process of modifying the surface of the substrate:

a) immerse a substrate for 30 seconds in a mixture consisting of hydrofluoric acid (40%), nitric acid (65%) and distilled water in a ratio of (1:4:5) and then rinse distilled water;

b) rinse with distilled water for 10 minutes in the ultrasound bath at room temperature;

c) dry stream of inert gas (argon).

- Carry out a process of vapor deposition according to the parameters of the process suitable for the corresponding precursor

Conditions	**(1)**	**(2)**
Precursor mass (m_p) [mg]	1 – 10	5 – 20
Sublimation temperature (T_S) [K]	523 563	423 – 463
Deposition temperature (T_D) [K]	533 – 563 603	483 – 563
Pressure (p) [mbar]	3 – 4	1,5
Time (t) [min]	30 - 60	45 – 90

- subject the layers to structural analysis (XRD) and studies on morphology (SEM/TEM).

The report of the exercise:

- Describe the process of deposition of silver from gas phase.
- Analyze the structural layers based on XRD data.
- Analyze the surface morphology on the basis of data from electron microscopy.

Laboratory 4/5

The study of the photocatalytic activity of titanium dioxide coatings obtained by chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques

Dr A. Radtke

Thin films and coatings are used in nearly all fields of modern technology in a wide variety of applications. For example microelectronic devices (microprocessors, memories) have been prepared using thin film technologies. Also many optoelectronic devices, like flat panel displays and semiconductor lasers are based on thin films. Other application areas include solar cells, various detectors (heat, gas, pressure, acceleration), optics, biomaterials, and protective and decorative coatings. Thin films are prepared with both chemical and physical methods. In the chemical methods the thin film material is produced in the deposition process through chemical reactions, while in the physical methods the film forming material is transferred from source to the substrate by physical means. Chemical methods can be divided further to liquid and gas phase methods depending on the phase through which the precursors are brought onto the substrate surface.

Titanium dioxide TiO_2 is a versatile material that is used especially as a white pigment. TiO_2 has also many thin film applications in optics, micro- and optoelectronics and as protective coating in for example biomaterials where the non-toxicity and biocompatibility of TiO_2 are important. During the past years TiO_2 has gained a lot of attention as a photocatalytic material that decomposes organic matter. When TiO_2 is illuminated with UV-light whose energy is larger than the band-gap of TiO_2 (3.1-3.3 eV), the light is absorbed into TiO_2 producing electron-hole pairs which through a chain of reactions decompose organic compounds on the surface of TiO_2 and in its vicinity (Fig. 1). Another remarkable effect of UV-light is the conversion of TiO_2 surface to superhydrophilic: water droplets tend to spread on an illuminated surface as a continuous layer. The process leading to superhydrophilicity involves formation of oxygen vacancies on the surface that subsequently become filled with hydroxyl groups when water is dissociatively adsorbed on the surface (Fig. 2). The photocatalytic and superhydrophilic properties make TiO_2 coated window glass self-cleaning: during a sunny day organic contaminants are degraded photocatalytically and during a rainwater rinses possibly remaining degradation products and other solid contaminants. Besides windows, self-cleaning TiO_2 coatings are used in also other construction materials and for example in lamp covers of highway tunnels. Photocatalytic TiO_2 has been used also as self-sterilizing coating and in air and water cleaning.

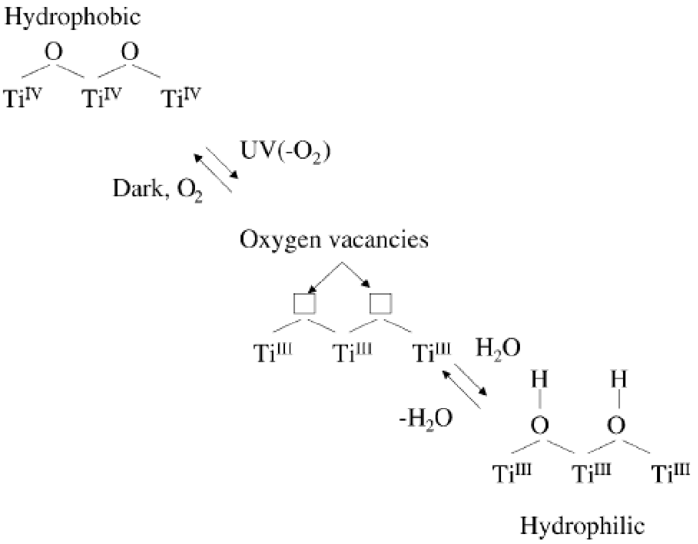

Fig. 1. Principle of photocatalytic degradation of organic compounds. When absorbed into TiO_2 a photon produces an electron-hole pair. After diffusing to the surface the hole oxidises -Ti-OH surface species into hydroxyl radical Ti-OH+• which in turn may oxidise organic compounds to carbon dioxide and mineral acids. A hydroxyl radical may also form when the hole reacts directly with a water molecule. An electron excited into the conduction band of TiO_2 can reduce an adsorbed O_2 molecule into superoxide radical which can reduce further into hydrogen peroxide. Hydroxyl radicals may also form as intermediates of this process. These all are strong oxidizing agents.

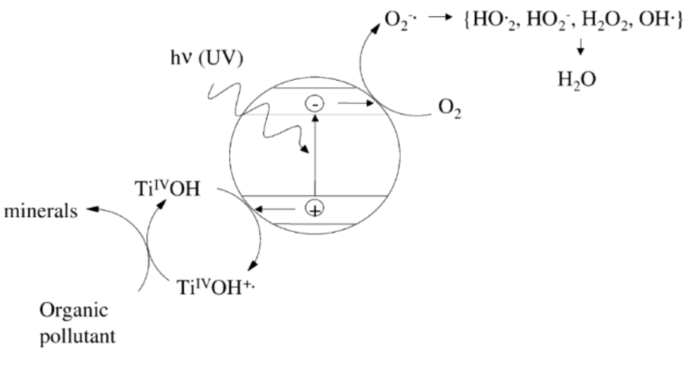

Fig. 2. A mechanism producing the photoinduced superhydrophilicity. In dark a reverse process takes place slowly.

Thin films and coatings of TiO_2 may be obtained in many ways. During the laboratory exercise, TiO_2 layers obtained by CVD and PVD will be used. Photocatalytic activity of TiO_2 layer will be examined on the base of the degradation of the methylene blue aqueous solution and the degradation of the stearic acid as the organic layer on the surface of titanium dioxide. Superhydrophilicity will be also analyzed. All experiments will be carried out after irradiation with UV light.

Objective of the exercise:

- To determine and compare the photocatalytic activity of TiO_2 layers obtained by two different methods vapor deposition (CVD and PVD)
- To familiarize with the DRIFT IR method and to analyze with DRIFT spectra used for stearic acid, degraded on the surface of TiO_2
- To be acquainted with spin coating method used for the deposit a layer of stearic acid on a thin coating of titanium dioxide

Materials and reagents:

- TiO_2 layers obtained by CVD and PVD methods - differing in structure, morphology and thickness
- Stearic acid
- Methylene blue
- methanol

Apparatus:

- Analytical balance
- 500ml round bottom flask
- Metal Tweezers
- Plastic cuvettes
- UV-Vis spectrophotometer Metertech SP-830 PLUS
- IR SPECTRUM 2000 spectrophotometer with an attachment DRIFT
- A spin-coater
- Apparatus for measuring the contact angle Kruss
- Emita UV lamp
- Beakers
- Pasteur pipettes

Exercise performance:

1. Degradation of methylene blue (BM)

- In a 500 ml volumetric flask, prepare a solution with a concentration of BM - $1{\cdot}10^{-5}$ M,
- Register the output spectrum of a solution of BM in the visible range (400-800 nm) using distilled water as a reference and using plastic cuvettes,
- Determine the characteristic band of BM,
- Put the CVD / PVD TiO_2 layer deposited on a substrate (Ti or Al), with dimensions of 5mm · 5mm, into the plastic cuvettes,
- Fill the cuvettes with BM solution using a Pasteur pipette,
- Cuvettes with the solution of the BM and with inserted layers of TiO_2 place under UV lamp, writing distance between the lamp and the TiO_2 layer,
- Expose cuvettes with the solution of the BM layer and the introduced TiO_2 for 10 minutes and after this time, measure the absorbance at a wavelength determined previously (characteristic band of BM),
- Keep irradiation of UV and measure absorbance of the BM solution successively every 10 minutes untill the end of the laboratory exercise.

2. Degradation of stearic acid (SA)

- In a volumetric flask for 100 ml, prepare a solution of stearic acid in methanol, with a molar concentration of $8.8 \cdot 10^{-3}$ M,
- Using a spin-coater, deposit a layer of stearic acid on the TiO_2 layer; for this purpose, place a few drops of the solution of SA on a TiO_2 layer and set on a spin-coater the conditions of deposition: 1000 min^{-1}, time - 1 minute,
- Dry the applied layer using argon,
- Register the spectrum of substrates with a layer of TiO_2 and TiO_2 coated with stearic acid, using for this purpose an attachment DRIFT (in the presence of an assistant of exercises),
- Expose the substrate with a layer of TiO_2 coated with stearic acid on UV light and record the spectrum, every 15 minutes, in the range of 400-4000 cm^{-1} using an DRIFT IR.

3. Analysis of the contact angle / hydrophilicity of TiO_2 layers

- Using a camera to measure the contact angle test the degree of hydrophilicity of TiO_2 layer prior to irradiation with the UV radiation, and after irradiation with UV lamp (measure every 5-10 minutes – time established with a supervisor of exercise).

Report of the exercise:

- Describe the procedure for preparation of TiO_2 layers by chemical or physical vapor deposition (to be agreed with the supervisor exercises).
- Define the photocatalytic activity of TiO_2 layers based on:
  (a) degradation of the BM (plot the dependence between the absorbance of BM analytical band and UV irradiation time),
  (b) degradation of the SA (plot the dependence between the surface area of the vibration bands of the stearic acid C-H and UV irradiation time)
- Analyse photoinduced hydrophilicity of TiO_2 layer on the basis of the measurements of contact angle.

Laboratory 6

Modification of montmorillonite by alkali metal ions (4 versions)

Prof. dr hab. H. Kaczmarek, Dr T. Czerniawski

The purpose is to understand how to modify the montmorillonite by sodium or lithium ions (using a magnetic or mechanical stirrer)

Reagents:

- NaCl pure (versions 1a and 1c) or LiOH · H_2O pure (versions 1b and 1d)
- Montmorillonite (MMT)
- $AgNO_3$ (solution)
- Universal indicator paper

Equipment:

- magnetic stirrer (version 1a and 1b) or repulsion stirrer (version 1c and 1d)
- support stand, clamps
- flask (V = 250 ml)
- autotransformer
- thermometer
- 600 ml beaker
- centrifuge,
- laboratory and analytical balance
- drier
- heating jacket
- weighing dishes
- crystallizer

How to conduct the experiment:

Prepare an aqueous solution of NaCl (version 1a and 1c) and LiOH (version 1b and 1d) at a concentration of c = 1 mol / l using a volumetric flask (V = 250 ml). Weigh 1.25 g montmorillonite on analytical balance.

Versions 1a and 1b

Build a reaction set consisting of a magnetic stirrer (connected to the 220 V through an auto-transformer), a beaker and a thermometer held in the paw tripod. Pour the NaCl solution into a beaker, start mixing and keep the temperature around 70 - 80 ° C by means of the autotransformer. Enter MMT and stir for 1 h, keeping the temperature as above.

Versions 1c and 1d

Build a reaction assembly consisting of a mixer and three-necked flask equipped with a glass stirrer with a seal, a thermometer and a reflux condenser. Pour NaCl to flask, mount heating montle (connected to 220 V by the autotransformer), start mixing and keep the temperature around 70 - 80°C. Enter MMT and stir for 1 h, keeping the temperature as above.

After heating, centrifuge modified montmorillonite at least three times. Wash the precipitate with distilled water until disappearance of chloride ions in the case of Na-MMT or to obtain a neutral environment in the case of Li-MMT. Move the product to a crystallizer, dry - initially in air and then place in an oven at 60°C and leave for the next week. After thorough drying, weigh and evaluate efficiency.

Results elaboration (performed by the students at home and delivered to the next class) should include the following elements:

1. Title, date and place of exercise performance
2. The names of the persons whose did exercise
3. Definition of the composite and the nanocomposite
4. Short characteristics of polymer nanocomposites
5. Montmorillonite: structure, formula, occurrence, properties, applications
6. Purpose of the exercise
7. Description of exercise with own observations
8. Signatures of students

Laboratory 7

Modification of montmorillonite by aliphatic or aromatic amines (4 versions)

Prof. dr hab. H. Kaczmarek, Dr T. Czerniawski

The aim of the task is to learn the methods of Li-MMT or Na-MMT modification using quaternary aliphatic or aromatic amines.

Reagents:
- aliphatic amine - methyltrialkyl(C_8-C_{10})ammonium chloride (*version 2a and 2b*) or aromatic amine – benzyltributylammonium chloride (BTBA) (*version 2c and 2d*)
- montmorillonite: Na-MMT (*version 2a and 2c*) or Li-MMT (*version 2b and 2d*)
- $AgNO_3$ (solution)

Equipment:
- magnetic and repulsion stirrer
- support stand, clamps
- three necked flask
- autotransformer
- thermometer
- 100 ml beaker
- measuring cylinder
- centrifuge,
- analytical balance
- drier

How to conduct the experiment

Weigh sodium or lithium containing montmorillonite (Na-MMT- *version 2a* and *2c* or Li-MMT - *version 2b* or *2d*) on analytical balance (m = 5,00 g).

Build a reaction assembly consisting of a stirrer, three-necked flask equipped with a glass stirrer and a glass seal, a thermometer and a reflux condenser. Pour 100 ml of distilled H_2O into three-necked flask of and add the weighed Na- MMT or Li-MMT. Start the mixing keeping the temperature around 70 - 80°C by means of an autotransformer. On an analytical balance, weigh 2.25 g of a quaternary amine (Adogen

® 464 or BTBA), transfer to a beaker of 100 ml capacity, and add 25 ml of distilled H_2O. Heat to a temperature of 70 ÷ 80 ° C and mix continuously. The beaker with amine transfer to a three-necked flask. Stir for 1h and maintain the above temperature. Then, centrifuge the modified montmorillonite few times, washing with distilled water until disappearance of Cl-ions. Place the product into the weighing dish, dry in air and then - in an oven at 60°C. Leave for complete drying to the next class; weigh after thorough drying.

Preparation of solutions to the next class

Prepare 100 ml polymer solution (having a concentration of 2% m/v) in a volumetric flask. Kind of polymer is indicated by the teacher. Do not fill up the flask to the mark! Allow to dissolve the polymer completely and only then make up to the mark with solvent.

The following water-soluble polymers are available:
poly (ethylene oxide), PEO
polyvinylpyrrolidone, PVP
poly (acrylic acid), PAA
poly (ethylene glycol) PEG;
and poly (methyl methacrylate), PMMA - soluble in toluene,

Caution!
Toluene is toxic solvent! Refer to the safety data sheet [of the Charter of the characteristics of hazardous substances such as http://www.poch.com.pl].
Be careful, work in a fume cupboard, use goggles and gloves!

Results elaboration (performed by the students at home and delivered to the next class) should include the following elements:

1. Title, date and place of exercise performance
2. The names of the persons whose did exercise
3. Purpose of the exercise
4. Chemical structure of applied amine
5. Chemical structure of modified montmorillonite.
6. Predicted properties of obtained nanocomposite
7. Description of exercise with own observations
8. Signatures of students.

Laboratory 8

Preparation of montmorillonite nanocomposite polymer by a solvent method (two versions, five different polymers)

Prof. dr hab. H. Kaczmarek, Dr T. Czerniawski

The purpose is to obtain a nanocomposite with a modified montmorillonite in the polymer solution.

Reagents:

- The selected polymer: poly (ethylene oxide), PEO, poly (acrylic acid), PAA, poly (methyl methacrylate), PMMA, polyvinylpyrrolidone, PVP or poly (ethylene glycol) PEG;
- Montmorillonite modified by the addition of 25-30% octadecyl trimethyl ammonium chloride (Nanomer ® 1.28);
- Solvent - distilled water or toluene;
- Ethanol (to precipitate the PMMA nanocomposite).

Caution!
Toluene is toxic! Refer to the safety data sheet. Be careful, work in a fume cupboard, use goggles and gloves!

Equipment:

- magnetic stirrer
- autotransformer
- evaporator
- 100 mL beaker
- 300 mL conical flask
- 100 mL measuring flask
- ultrasonic cleaner
- thermometer
- centrifuge,
- vaccuum drier
- evaporator
- analaytical balance
- support stand, clamps, connectors.

How to conduct the experiment:

To perform a task, 100 ml of polymer solution (c = 2% m/v) prepared in the previous class is needed.

The procedure in the case of water-soluble polymers (*version 3a*)

In the beaker of 100 ml volume, weigh of 0.10 g the modified montmorillonite (Monomer ® 1.28) on an analytical balance. Add 50 ml of distilled water and stir with a magnetic stirrer maintaining a temperature of 60 ÷ 70°C. The polymer solution and MMT dispersion move into a conical flask and place in an ultrasonic bath for 1h. Then, centrifuge an excess ("unreacted") MMT, and evaporate the solvent from solution (in the fume hood). Alternatively, you can use the evaporator. Continue drying to constant weight in a vacuum oven.

The procedure in the case of PMMA soluble in toluene (*version 3b*)

In the conical flask of 100 ml capacity, weigh 0.10 g Nanomer® 1.31PS (montmorillonite modified by 15 -35% octadecylamine) on an analytical balance. Add 50 ml of toluene and stir using a magnetic stirrer, at 60 ÷ 70°C. Transfer a solution of the polymer (PMMA) and MMT (nanomer ® 1.31PS) dispersion to a 300 ml conical flask and place in an ultrasonic bath for 1 hour. Then, pour the entire content of the flask into a beaker with a capacity of 800 ml, containing 400 ml of ethanol. Stir. Centrifuge the precipitated polymer nanocomposite and dry in a fume cupboard weighing.

Results elaboration (performed by the students at home and delivered to the next class) should include the following elements:

1. Title, date and place of exercise performance
2. The names of the persons who did exercise
3. Substances used and theirs chemical formulae.
4. Information on toxic properties of toluene and precautions when working with this solvent.
5. Main properties and application of the polymer under test.
6. Projected construction of the resulting nanocomposite.
7. The proposals of properties studies and identication of nanocomposite structure.
8. Description of exercise with own observations.
9. Signatures of students.

Laboratory 9

Preparation of polymer nanocomposite with montmorillonite by *in situ* method (4 versions, 4 types of MMT)

Prof. dr hab. H. Kaczmarek, Dr T. Czerniawski

The aim of the study is the polymerization of methyl methacrylate in the presence of modified montmorillonite in order to obtain the polymeric nanocomposite.

Reagents:

- monomer – freshly distilled methyl methacrylate (MMA)
- initiator - ammonium persulfate $(NH_4)S_2O_8$ or 2,2’- azobisisobutyronitrile) AIBN
- differently modified montmorillonite; choice includes:
  Z-MMT-1 (Na-MM-Adogen®464); Z-MMT-2 (Li-MM-Adogen®464), Z-MMT-3 (Na-MMT-BTBA), Z-MMT-4 (Li-MMT-BTBA), Adogen®464 - methyltrialkyl(C_8-C_{10})ammonium chloride, BTBA - benzyltributylammonium chloride;
- ethanol

Equipment:

- repulsion stirrer
- autotransformer
- thermometer
- three necked flask (250 ml)
- 100 ml measuring flask
- reflux
- heating jacket
- centrifuge
- drier
- balance
- support stand, connectors, clumps

How to conduct the experiment:

In a volumetric flask, prepare 100 ml of an ethanol solution of methyl methacrylate (MMA molar mass = 100.12 g / mol) with a concentration of c = 4.0 mol/l.

Weigh on an analytical balance 0.10 g of the modified montmorillonite. Build a reaction assembly consisting of the stirrer, 250 ml three-necked flask, reflux condenser and thermometer. Pour the solution of the monomer (MMA); add montmorillonite (MMT-Z-1, Z-MMT-2, Z-MMT-3 or Z-4-MMT) to a reaction flask. Turn on the mixing and heating jacket, maintaining the temperature at 60°C with autotransformer. On an analytical balance, weigh the appropriate amount of initiator. Use 0.6 to 0.7 g of ammonium persulfate or proper amount of AIBN (to its concentration of 0.01 mol/l, AIBN molar mass = 164.2 g / mol). The weighed initiator transfer to the reaction flask and start polymerization, which should be carried out for 1h. Precipitated polymer nanocomposite wash with ethanol several times, each time after centrifugation. Transfer the product to a weighing dish and place in an oven at 40°C.

Results elaboration (performed by the students at home and delivered to the next class) should include the following elements:

1. Title, date and place of performance of exercise
2. The names of the persons whose did experiment.
3. A brief description of the free-radical polymerization mechanism
4. Information on toxic properties of monomer used.
5. The chemical formula of the monomer and nanomodifier used.
6. Predicted structure of the resulting nanocomposite.
7. Methods of investigation of nanocomposite structure.
8. Description of exercises with own observations
9. Signatures of students

Preparation to the next class

Preparation of polymer and nanocomposite films (for Exercise 5) by casting method and evaporation of the solvent:

In the flasks with a capacity of 25 or 50 ml, prepare two solutions: starting unmodified polymer and the polymer nanocomposite of 2% (m/v). The solvent is water or toluene depending on the type of polymer (the same as in exercise 2). The solutions of the pure polymer and nanocomposite cast onto a glass plate or leveled Petri dishes (using 25 ml of solution per 100 cm^2 surface) and allow evaporating the solvent. Then, place the films to the vacuum oven for complete removing of the residual solvent.

Laboratory 11

The study of the mechanical properties of polymer nanocomposites

Prof. dr hab. H. Kaczmarek, Dr T. Czerniawski

Aim of this study is to investigate the mechanical properties of nanocomposite polymer and unmodified polymer using tensile test machine INSTRON

Reagents:

Samples of the polymer nanocomposite and unmodified polymer taken alone or provided by the teacher.

Equipment:

- Tensile testing machine Instron Model 1026,
- Micrometer screw,
- Caliper

How to conduct the experiment:

Polymer nanocomposite and starting, unmodified polymer films, prepared earlier, remove gently from the substrate, and then cut 5-10 fittings (standard dumbbells) using punch and by mechanical press. Measure the exact thickness of each sample at approximately 10 points by micrometer screw and calculate the average value. Measure the length of the test section using caliper. Place the dumbbell specimen in the jaws crosshead and start the breaking. Record the breaking process (the relationship of the force versus deformation). Determine the tensile strength, elongation at break, and Young's modulus for both the starting polymer and the polymer nanocomposite. Calculate average values of all measured parameters for an each sample type. Calculate the standard deviation.

Results elaboration (performed by the students at home and delivered to the next class) should include the following elements:

1. Title, date and place of performance of exercise.
2. The names of the persons who did exercise.
3. Purpose of exercise.
4. The recorded curves, calculated values of mechanical parameters
5. The data in a table.
6. Compare obtained parameters for the polymer and a polymer nanocomposite.
7. Conclusions.
8. Signatures students

Table 1. Parameters characterizing the mechanical properties of the polymer samples

Sample	Tensile strength [MPa]	Ultimate elongation [%]	Young Modulus [MPa]
Polymer ...			
Standard deviation			
Nanocomposite ...			
Standard deviation			

Preparation to the next class

Using the available databases (NCU library, electronic resources, achievable after logging or open access journals), found in the scientific literature at least 1 publication on studying the structure of montmorillonite and its composites with a polymer concerning X-ray diffraction technique and 1 publication on the study of thermal properties of considered systems. Read these works. In the case of problems with the search of literature, contact to the teacher for consultations before class.

Laboratory 12

Investigation of thermal properties and X-ray structure of polymer nanocomposites with montmorillonite

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The aim of the work is:

- Interpretation of X-ray diffraction patterns of montmorillonite before and after modification, as well as after the introduction to polymer matrix;
- learning the thermogravimetric analysis on selected examples of polymer nanocomposites,
- determination of activation energy of thermal decomposition of the samples by the following methods: Horowitz–Metzger, Coats–Redfern, Kissinger, Flynn-Wall, Ozawa and Friedman.

Materials:

Publications found in the databases. X-ray diffraction patterns and thermogravimetric curves provided by the teacher. X-ray data of MMT.

The task implementation

X-ray diffraction analysis of MMT:

Read the position of 2Θ angle, where the signal appears. Calculate d-spacings from the Bragg equation. Compare the values for unmodified MMT and after the modification, and in the matrix polymer.

Analysis of the TG DTG, DTA curves:

1. Horowitz - Metzger and Coats - Redfern methods

From the TG and DTG curves appoint:

- temperature at the beginning (T_o) and end (T_k) of the decomposition process [ºC],
- temperature at maximum rate (T_{max}) [ºC],
- temperatures T_1, T_2, T_3, ... differing by 10ºC,
- temperature at which a sample loses 50% of the initial mass (T_{50}) [ºC],
- mass at the end of decomposition, m_k [mg],
- mass of the sample in T_{max}, m_{max} [mg],
- mass of the sample at temperatures (T_1, T_2, T_3, ...), m_t [mg].

Based on the read parameters, determine the order of reaction (n) using formula:

$$c_{\max} = (n)^{1/1-n}$$

Where c_{oax} is the degree of conversion at T_{ax}

$$c_{\max} = (m_{\max} - m_k)/(m_0 - m_k)$$

You can use the data in the table below:

c_{oax}	n
0,000	0
0,250	1/2
0,368	1
0,444	3/2
0,500	2
0,574	3
0,630	4
0,669	5
1,000	∞

Calculate the activation energy, E [kJ/mol]

For n = 1, use the formula:

$$\ln\ln[(m_0 - m_k)/(m_t - m_k)] = E * \Theta / RT_{\max}^2$$

Where $\Theta = T - T_{\max}$

Plot a graph of the $\ln\ln[(m_0 - m_k)/(m_t - m_k)]$ versus Θ, and calculate the activation energy as tangent of the angle of slope.

For $n \neq 1$, use the formula:

$$\ln\{1 - [(m_t - m_k)^{1-n}/(m_0 - m_k)^{1-n}]/[1-n]\} = E\Theta / RT_{\max}^2$$

2. Kissinger, Flynn-Wall, Ozawa and Friedman method

Make a full analysis of the thermogravimetric curve of the polymer (provided by the teacher) using a computer program Universal Analysis 2000 (TA Instruments). Analyze the DTA curve and find the endo or exothermic effects.

Appoint following parameters from the TG and DTG curves:

- temperature at the beginning (T_o) and end (T_k) of the decomposition process [ºC],
- temperature at maximum rate ($T_{\max}$) [ºC],
- temperatures T_1, T_2, T_3, ... differing by 10ºC,
- temperature at which a sample loses 50% of the initial mass (T_{50}) [ºC],

- mass at the end of decomposition, m_k [mg],
- mass of the sample in T_{max},, m_{max} [mg],
- mass of the sample at temperatures (T_1, T_2, T_3, ...), m_t [mg].

Using MS Excel spreadsheet determine the apparent activation energy of thermal decomposition of the polymer by following methods: Kissinger, Flynn-Wall, Ozawa and Friedman, using the formulas presented in the introduction to exercise. Compare the results obtained by various methods.

Report should include:

1. Title, date and place of performance of exercises.
2. The names of the persons who did exercise.
3. Purpose of exercise.
4. Literature data and summarized most important conclusions of published work on the structure and thermal properties of MMT and MMT-polymer nanocomposite. The formula of described polymers.
5. Description of the results of the XRD and thermogravimetric analysis. Type of the instruments and measurement conditions (teacher indicates the source).
6. On the basis of the literature data, assign the observed steps of thermal decomposition to suitable reactions.
7. List the data in the tables.
8. Compare the results of your own analysis to results from publications.
9. Draw conclusions.
10. Sign report.

Table 1. Results of X-ray diffraction of MMT and MMT nanocomposite.

Sample	Signal 2Θ, [°]	d-spacing, d[Å]
Polymer ...		
MMT unmodified		
Na-MMT or Li-MMT		
MMT modified with aliphatic or aromatic amine		
Nanocomposite ...		

Table 2. Thermal parameters obtained from thermogravimetric analysis of the polymer and nanocomposite (in case of more than one stage, the parameters for all stages).

Sample	Polymer ...	Nanocomposite...
Temperature of decomposition onset, T_o [°C]		
Temperature at maximum process rate, T_{max} [°C]		
Temperature at end of decomposition, T_k [°C]		
Mass loss, [%]		
Organic/inorganic residue, [%]		
Endothermic/exothermic effect range and temperature at maximum or minimum)		
Activation energy [kJ/mol]		
Coats – Redfern method		
Kissinger method		
Flynn-Wall method		
Ozawa method		
Friedman method		