JOINT CONFERENCES
ON ADVANCED MATERIALS AND TECHNOLOGIES

The 16th Conference
on Functional and Nanostructured Materials

FNMA'19

The 9th International Conference
on Physics of Disordered Systems

PDS'19

31 August – 7 September 2019
Athens and Agi Teodori, Greece

ABSTRACT BOOK

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THE 9th INTERNATIONAL CONFERENCE ON PHYSICS OF DISORDERED SYSTEMS

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CONTENTS

Oscillatory kinetics in nitriding process of nanocrystalline iron

W. Arabczyk, K. Skulmowska and E. Ekiert

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The industrial prereduced iron ammonia synthesis catalyst, KM1R (nanocrystalline iron promoted with hardly reducible oxide of aluminum 3.3 wt.%, calcium 2.8 wt.%, and potassium 0.65 wt.%), was applied in the study. The average size of iron nanocrystallites, as determined by the X-ray diffraction (XRD) method, was 45 nm [1]. The test sample consisted of a set of nanocrystallites described by their size distribution, CSD (crystalline size distribution) [2, 3]. The specific surface area of the sample, as determined by the thermal desorption, was 12 m^2/g. The surface was partially covered by the oxide of the promoters; thereby, the active surface area was smaller than the specific surface area, and its value depended on the temperature [4, 5].

The studies were carried out in a differential reactor equipped with a means for thermogravimetric measuring of the sample weight and a hydrogen analyzer. A sample of the catalyst was placed as a single layer of grains (1.0 to 1.2 mm diameter) in a platinum basket of the reactor suspended on a shoulder of the thermobalance. The flow rate of gases (ammonia, hydrogen, and nitrogen) was determined using automatic electronic controllers. Gas samples were taken for analysis in the immediate vicinity of the sample. The weight change of the sample, the temperature, and the partial pressure of hydrogen at the outlet of the reactor were recorded digitally [6].

Nitriding processes of nanocrystalline iron were carried out isothermally at 648, 623 and 598 K, at a variable nitriding potential until a steady state was established, during which the measured hydrogen concentration in the reactor was constant and the nitriding reaction rate was zero. At each temperature of the nanocrystalline iron nitriding processes, nanocrystalline iron nitrides with different nitrogen content were obtained [7, 8]. Under these conditions, nanocrystallites undergo phase transformation in the order from the smallest to the largest [9–11].

An example of the dependence of concentration of nitrogen in the sample and the concentration of the individual components in a gas phase on time and the change in the nitriding potential for the nanocrystalline iron nitriding process at 648 K are shown in Figure 2. For the dependence of the hydrogen concentration on time (Figure 2), the value at which the hydrogen concentration corresponding to the minimum nitriding potential, P_0, at which the phase transformation in the nanocrystalline iron nitriding process begins was reached is marked with the black point. Based on the results of thermogravimetric measurements and determining the hydrogen concentration in a gas phase, taking into account the mass balance of the reactor with perfect

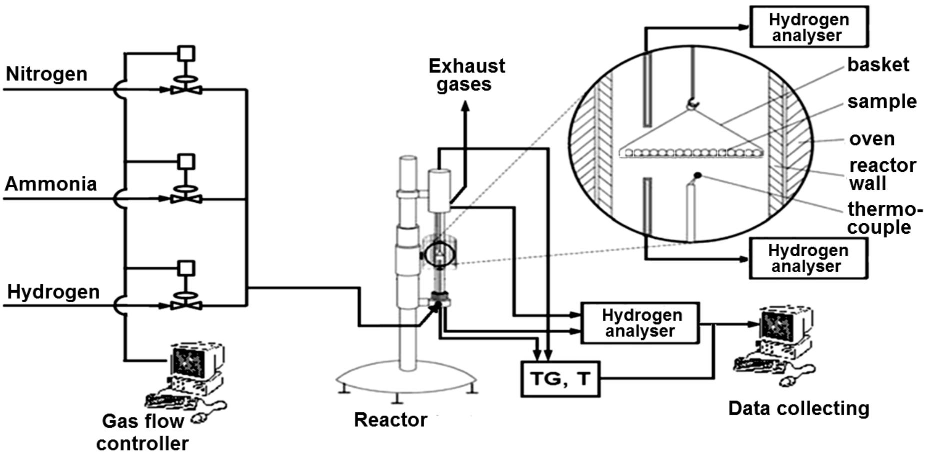

Figure 1. Apparatus setup

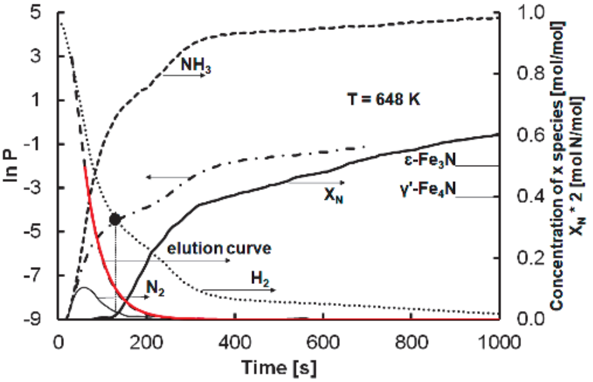

Figure 2. Dependences of nitrogen concentration in the sample, concentrations of hydrogen, ammonia and nitrogen and the nitriding potential on time of the nanocrystalline iron nitriding process (100% ammonia at the reactor inlet) at 648 K. Continuous red line – model results of the elution curve

mixing, the ammonia and nitrogen concentrations and the nitriding potential were calculated at each process step. Figure 2 shows also the dependence of the hydrogen concentration on time (the so-called “elution curve”).

Based on the dependences of the nitrogen concentration in the sample on the time of the nanocrystalline iron nitriding, the rates of this process were calculated as shown by the time for the temperatures of 648 and 598 K in Figure 3. The occurrence of oscillatory reaction rate changes was observed for the dependence of the nanocrystalline iron nitriding process rate on the process time. These oscillations were observed throughout the temperature range under investigation. A time shift in the occurrence of the maxima related to the process temperature was observed.

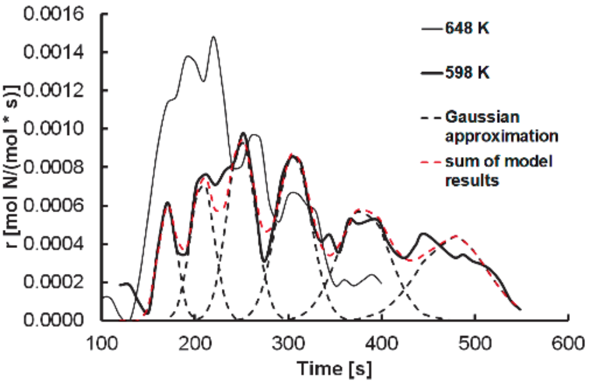

Figure 3. Dependences of the nitriding rate of nanocrystalline iron at 598 and 648 K on time. The red dashed line indicates the total reaction rate resulting from the proposed model

A similar phenomenon was observed for the reduction process of the nanocrystalline iron nitride γ'-Fe_4N. Every single cycle of oscillation corresponds to the transformation of the whole sample to the metastable state, where FeN_x is formed. The oscillations result from overlapping distributions of the crystallite size of a given sample.

Acknowledgements

The scientific work was financed by the National Science Centre, Poland – the Opus Program, Project No. 2017/27/B/ST8/02947.

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The effect of potassium content in nanocrystalline iron on its transition process

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Nanocrystalline iron doped with hardly reducible oxides of aluminum (2.6 wt.%), calcium (2.7 wt.%) and differing in the potassium oxide content 0.65 wt.% and 0.1 wt.% as well as in the specific surface area 12.5 m^2/g and 15.3 m^2/g was nitrided at 475°C under ammonia atmosphere on the terms of kinetics parameters *i.e.*, when the nitriding potential is much larger than the equilibrium potential, $P_N \gg P_N^{eq}$. The nitriding processes were studied in a differential reactor completed with systems that made it possible to investigate both the thermogravimetric measurements and the hydrogen concentration in the reacting gas mixture. The nitriding processes were preceded by a reduction of the passive layer with hydrogen (9 $dm^3h^{-1}g^{-1}$) at 500°C.

During the nitriding processes two parallel reactions occur:

- a nitriding reaction, formation of a solid solution of nitrogen in nanocrystalline iron (α – Fe(N)) and the next phase transition to iron nitride γ' – Fe_4N;
- a surface reaction of catalytic ammonia decomposition.

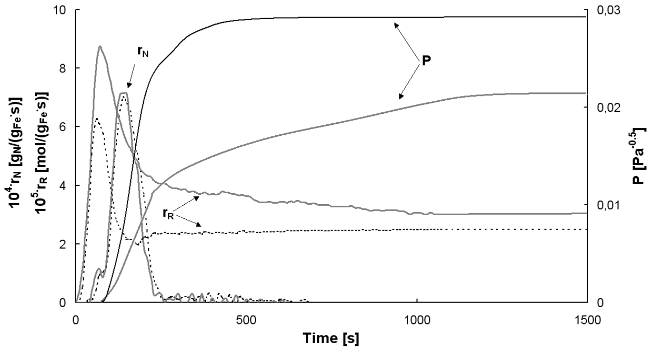
The time-dependences of the nitriding degree ($X_{N/Fe}$), the elution curve (exchange of hydrogen to ammonia in the reactor reaction volume) and the hydrogen concentration in a gas phase at the reactor outlet for the nanocrystalline iron nitriding process are presented in Figure 1a. It was found that the nitriding process occurred under unstable conditions wherein the nitriding potential and the rates of both reactions changed non-monotonically until a stationary state was reached after about 1000 s. During this particular state it is only the catalytic ammonia decomposition reaction that runs at a constant rate. It was assumed that there existed a chemical equilibrium between gas and solid phases in the stationary states.. Both samples were nitrided to a nitriding degree which exceeds the stoichiometric composition of the γ' – Fe_4N phase whereas the sample with a lower content of potassium oxide reached a larger nitriding degree.

Based on Figure 1a the reaction rates of the nitriding (r_N) and ammonia decomposition (r_R) were calculated (Figure 1b). The material balance of the reactor with an ideal mixing was calculated using both these rates as well as the rate of hydrogen elution from the reactor volume ($r_{elution}$):

$$r(X_{H2}^{N+R}) = r_N + r_R - r_{elution} \tag{1}$$

The values of the nitriding potential ($\mathrm{P_N}$) were calculated on the basis of the balanced concentrations of the gas components, (Figure 1b). It was evidenced that the sample with the smaller specific surface area required a smaller nitriding potential to undertake the phase transitions.

(a)



(b)

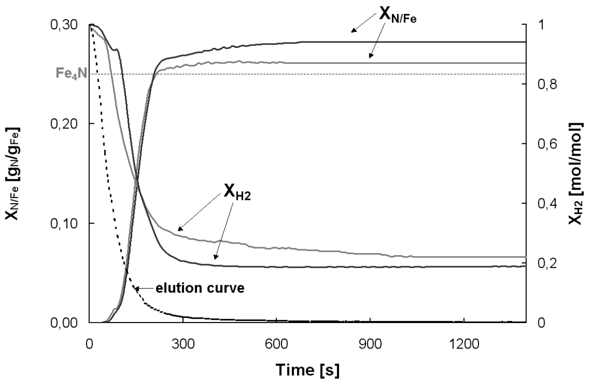


Figure 1. Time-dependences of: (a) the nitriding degree, the elution curve and outlet concentration of hydrogen in a gas phase (b) reaction rates of nitriding and ammonia decomposition for nanocrystalline iron nitriding processes; the sample with the 0.65 wt.% potassium oxide content was marked with grey lines, the sample with the 0.1 wt.% potassium oxide content was marked with black lines

The non-monotonic dependence between the nitriding reaction rate and the nitriding degree is shown in Figure 2a. It can be clearly seen that the chemical composition causes differences in this dependence.

The changes of concentration of active sites ($\mathrm{X_{act}}$) as a function of the nitriding degree are obtained (Figure 2b) from the following equation:

$$\frac{\mathrm{r_N}}{k \cdot S \cdot \mathrm{P_N}} \approx \mathrm{X_{act}} \cdot \mathrm{f}(\mathrm{X_{N/Fe}}) \tag{2}$$

where k – the constant reaction rate, S – the specific surface area for each sample.

On the basis of this Figure it was proposed that the initial peak (marked as $*$) was connected with the ammonia adsorption process. This dependence is approximately linear for $X_{N/Fe} > 0.05$ mol_N/mol_{Fe}, therefore the ratio of concentration of active sites for both samples was calculated from the slope of the extrapolated curve $(X_{act}^{0.65K_2O}/X_{act}^{0.15K_2O} \approx 2.7)$. It was concluded that the relative active surface decreased twice along with a sixfold decrease in the potassium oxide content in nanocrystalline iron.

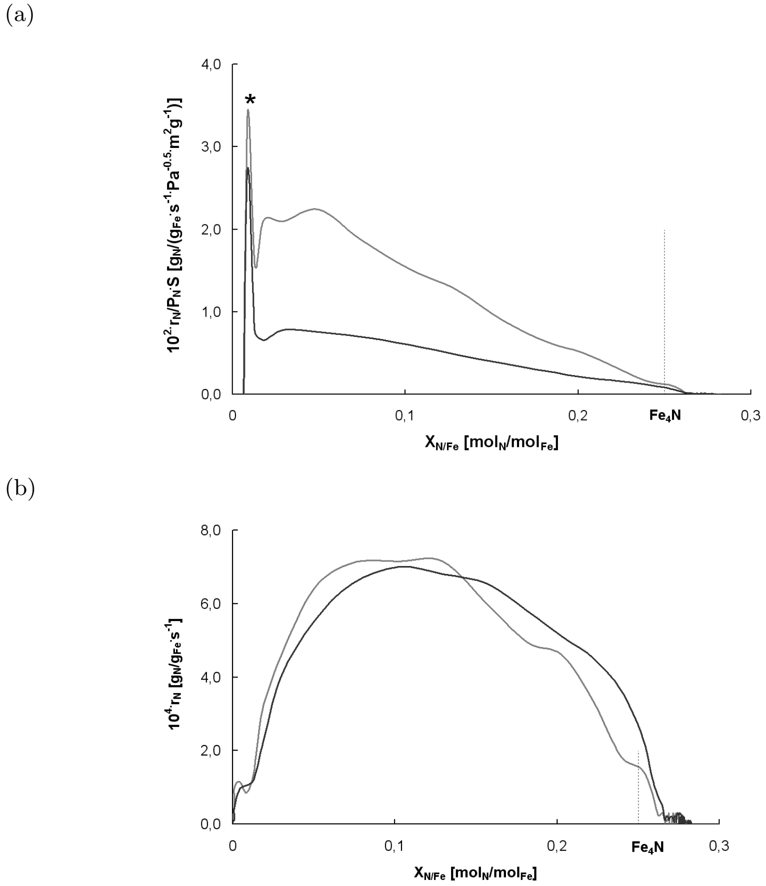


Figure 2. Nitriding degree-dependences of: (a) the nitriding reaction rate (b) concentration of active sites for nanocrystalline iron nitriding processes

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Modelling of networks exhibiting anomalous behaviour

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Through derivation of analytical models which describe the behaviour of various two and three-dimensional networks that deform through hinging and/or stretching, it is shown that it is possible to design systems which can achieve a set of specific mechanical properties, which may include negative Poisson's ratio and/or negative compressibility.

ABS04

EPR and DC magnetometry of Ni_2InVO_6

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A powder sample of Ni_2InVO_6 was investigated by electron paramagnetic resonance (EPR) and DC magnetometry. EPR spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 spectrometer operating at 9.5 GHz in the 4–300 K temperature range using an Oxford Instruments ESP helium-flow cryostat. The DC magnetization study was carried out using the MPMS XL-7 Quantum Design Magnetic Property Measurements System with a SQUID magnetometer in magnetic fields up to 70 kOe and in the 2–300 K temperature range. Since Ni_2InVO_6, which is isostructural with Ni_2FeVO_6, contains magnetic Ni^{2+} ($3d^8$) ions, its magnetic properties are worthy of being studied.

The EPR spectrum (see Figure 1) consisted of three weak and narrow lines (labelled A, B, and C) and one very broad resonance line (designated as D). Line A, located at g-factor equal to 4.25, displayed typical paramagnetic behaviour during the temperature change and is probably due to an unintentional admixture of high-spin ($S=5/2$) Fe ions located at axial sites with a strong rhombic distortion ($E/D \approx 1/3$). It is also line C may emerge from contaminated Fe ions, but located at axial symmetry sites without any significant distortion. Line B, at g-factor equal to 2.22, is most probably due to the separated Ni^{2+} ($S=1$) ions. As the D component in the EPR spectrum of Ni_2InVO_6 has a linewidth larger than the effective resonance field, its partner in negative magnetic fields must be considered in line fitting. The integrated intensity of line D increases with a temperature decrease down to ~ 15 K following the Curie-Weiss law with a positive Curie-Weiss temperature parameter indicating the presence of short-range ferromagnetic interactions. Below 15 K the integrated intensity of line D decreases with the decreasing temperature suggesting spin freezing in the antiferromagnetic system. The spectral characteristics of this component point out to nickel spin clusters as a possible source of line D.

The magnetic properties of Ni_2InVO_6 have been investigated previously by AC magnetic susceptibility and specific heat studies [1]. It has been found that the compound shows the spin-glass-like behaviour below the freezing temperature $T_f = 5$ K. A positive value of the paramagnetic Curie-Weiss temperature suggested ferromagnetic short-range interaction in the paramagnetic phase. The presence of antiferromagnetic-like correlations in Ni_2InVO_6 was indicated by a shift in the maxima toward

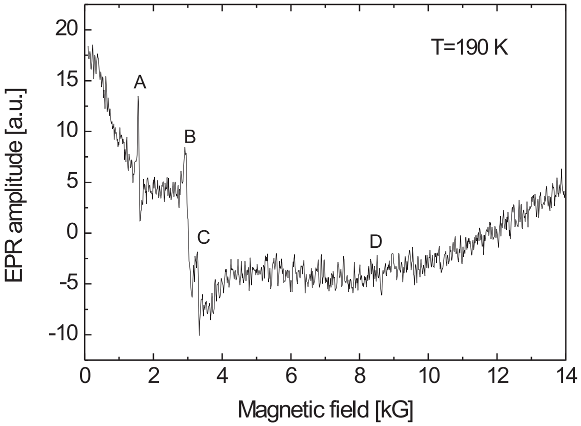

Figure 1. EPR spectrum of Ni_2InVO_6 registered at $T = 190$ K

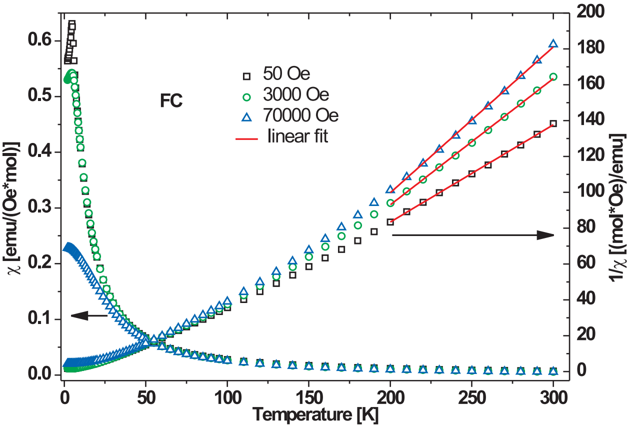

Figure 2. Temperature dependence of DC susceptibility (left axis) and reciprocal DC susceptibility (right axis) registered in three different applied magnetic fields in the FC mode. The solid straight lines at high temperatures are the least-squares fits to the Curie-Weiss law

lower temperatures in the specific heat $C(T)$ or $C(T)/T$ data during the magnetic field increase. Our DC magnetisation measurements confirmed, in general, this picture of the Ni_2InVO_6 magnetic properties, but there were also notable differences. In Figure 2 the temperature dependence of the DC susceptibility and reciprocal DC susceptibility registered in three different applied magnetic fields in the FC mode is shown. The solid straight lines at high temperatures are the least-squares fits to the Curie-Weiss law. The effective magnetic moment of the formula unit calculated from the Curie constant was in the range 3.1–3.8 μ_B (depending on the external magnetic field), which is significantly smaller than in [1] ($\sim 5\,\mu_B$). On the other hand, the calculated value of the Curie-Weiss temperature (50–80 K, depending on the magnetic field) was substantially higher than in [1] (5 K). A stronger ferromagnetic interaction and a smaller effective moment obtained from our DC magnetisation measurements demonstrate a substantial influence of local defects and imperfections on the global magnetic properties of Ni_2InVO_6.

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Networks with magnetic inclusions

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We discuss how the mechanical behaviour of a structure can be modified through the smart inclusion of magnets which may invert the properties of the structures to make them exhibit a variety of anomalous 'negative mechanical properties'.

Polarizable QM/MM based on linear-scaling DFT with *in situ* optimized localized basis functions and the AMOEBA force field

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Recently developed polarizable force fields, such as AMOEBA [1], improve over commonly used fixed-charge classical approaches by including many-body electrostatic effects. However, using QM/MM approaches remains necessary in cases where electron transfer is involved, *e.g.* in catalysis. The development of QM/MM approaches employing polarizable force fields is still at an early stage [2].

We describe TINKTEP [3, 3b]: a novel QM/MM approach based on the ONETEP [4] linear-scaling DFT formalism, and the polarizable force-field AMOEBA, as implemented in TINKER [5]. The QM and MM subsystems are coupled electrostatically and through van der Waals interactions. A generalization of distributed multipole analysis (DMA [6]) to localized orbitals optimized *in situ* is used to represent the QM density in terms of atom-centered multipoles for the sake of the QM/MM interface. The use of this auxiliary representation enables treating QM/MM polarization interactions on the same footing as intra-MM polarization. The polarization response of the MM subsystem is determined self-consistently using TINKER. The total energy expression, which we minimize using gradient methods, accounts for permanent electrostatic, polarization and van der Waals interactions between the two subsystems. The electrostatic coupling of QM and MM is a highly non-linear problem, with a requirement for both descriptions to achieve self-consistency. We show how this necessitates careful consideration of the coupling, its effects on energy gradients, and suitable damping of electrostatic interactions. We show how the use of *in situ* optimized localized basis functions improves the accuracy of the QM description, but also exacerbates difficulties, such as QM region overpolarization. We explain how these issues can be remediated. We validate the proposed approach on a number of model systems (both charge-neutral and charged), demonstrating its superiority over fixed-charge QM/MM approaches. We envisage that this method will be useful for a wide range of chemical and biochemical grand challenge simulations.

Acknowledgements

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Novel 2D and 3D auxetic and related structures

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We show that although the last decades have witnessed the development of a large variety of mechanisms which are conducive to auxetic and other negative behaviour, we are still able to create new and/or improved constructs, both in 2D and 3D, which may exhibit anomalous properties such as negative Poisson's ratio or negative compressibility. We also show how some of these systems can retain negative behaviour for relatively large deformations.

Polyphenylacetylene and polyphenyletylene networks with anomalous properties

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We present a comparison of the various families of two-dimensional polyphenylacetylene and polyphenyletylene networks with specific connectives. These networks have been specifically designed to mimic particular macrosystems which are known to exhibit unusual mechanical behaviour. We show, through molecular modelling, that in most cases (but not always), these nano-level systems are capable of replicating the mechanism that occurs at the macroscale and behave in a manner which is conducive to ‘negative mechanical behaviour’.

Properties of liquid crystalline ultra-thin films on the surface of carbon, silicon carbide and boron nitride nanostructures – computer simulation study

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Liquid crystals are a phase of matter that combines the mobility of an isotropic liquid with the long-range orientational order, which is normally associated with crystalline solids, and have been used for applications that rely on their anisotropic electrooptical properties. As the ordering of molecules is known to be essentially influenced by interfaces and dopants, anchoring of the liquid crystals and other functional organic molecules at a variety of interfaces has been studied for fundamental scientific reasons but also because the molecular organization of liquid crystals at their interfaces is essential for designing and optimizing a variety of optoelectronic devices and implementing new promising concepts in nano- and biotechnology [1]. Optical properties of thin molecular layers (*e.g.*, transparency) as well as the ability to switch between orientational configurations easily and in a controlled manner makes them good materials for display devices and transoptors. Anchoring of liquid crystals at their interfaces with such substrates as graphene, carbon nanotubes or polymer nanofibers proved to essentially affect their orientational order and their electrooptic and dielectric properties [2]. In this work, we studied properties of ultra-thin films of n-cyanobiphenyl (with $n = 5, \ldots, 8$) series of mesogens anchored on the surface of homogenous graphene and carbon nanotubes as well as their heterogenous silicon carbide and boron nitride counterparts in order to assess the impact of substrate morphology and polarization on the ordering and stability of these phases [3, 4].

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Anomalous mechanical behaviour in crystalline materials

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Simulations of crystalline materials using DFT and/or force-field based methods reveal how a number of such materials are capable of exhibiting anomalous mechanical behaviour, which include negative Poisson's ratio and/or negative compressibility.

Auxeticity though buckling

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This paper presents the results of simple experiments and simulations which show how auxeticity may be achieved as result forcing units of truss-like structures to move out-of-plane when uniaxially pulled. It is shown that this mechanism can be replicated at various scales of structure ranging from the macroscale to the nanoscale.

Localized magnetic moments in nitrogen-modified titanium dioxide

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The number of magnetic centers associated with trivalent titanium ions in the anatase phase increased over two orders of magnitude, while in the case of the rutile phase it decreased by the same order after annealing samples to a temperature in the 600°C and 650°C range. The N-TiO_2 photocatalysts that exhibited the weakest photocatalytic properties displayed also a very weak EPR spectrum arising from the trivalent titanium ions. The number of free radicals in the studied nanomaterials obtained at different annealing temperatures differed significantly. An increase in the number of trivalent titanium ions in the anatase phase was due to the transfer of electrons from the rutile to the anatase phase. Additionally, an increase in the number of trivalent titanium ions caused a decrease in the photocatalytic properties. At higher thermal annealing temperatures (over 800°C) where the rutile phase dominates, an increase in the intensity of the EPR spectrum of the trivalent ions of the titanium was observed by several orders of magnitude. For N-TiO_2 nanomaterials calcined at temperatures in the 600°C to 650°C range, the transfer of electrons from the anatase to the rutile phase was possible to observe and this transfer could enhance the photocatalytic efficiency. This transfer corresponds to an energy of about 0.3 eV.

ABS13

Magnetic resonance spectra of hybrid nanocomposites containing nanocrystalline TiO$_2$ and graphene-related materials

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Figures 1 and 2 present magnetic resonance spectra nanocomposites TiO$_2$-1ButOH (a), TiO$_2$-GO_5% (b) and TiO$_2$-1ButOH-GO_5% at liquid helium and room temperature. The preparation and description of the nanocomposites was reported in work [1]. Complex magnetic resonance spectra occurring with different magnetic centers are observed at low temperatures. Table 1 shows g_{eff} of the obtained resonance lines.

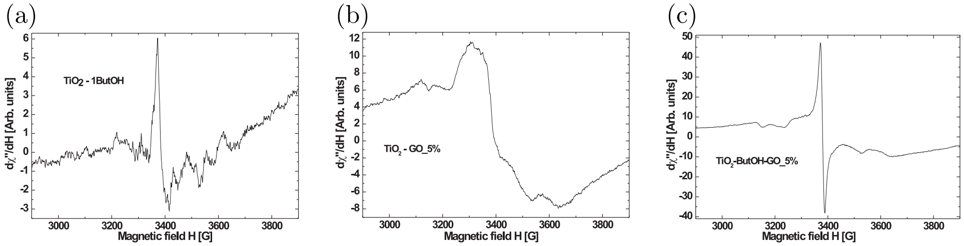

Figure 1. Magnetic resonance spectra at 4 K for: (a) TiO$_2$-1ButOH, (b) TiO$_2$-GO_5% and (c) TiO$_2$-1ButOH-GO_5%

The asymmetrical broad intense resonance line is observed in all nanocomposites at room temperature (Figure 2). The magnetic resonance parameters are shown in Table 2. The position of the resonance line is shifted to a lower magnetic field.

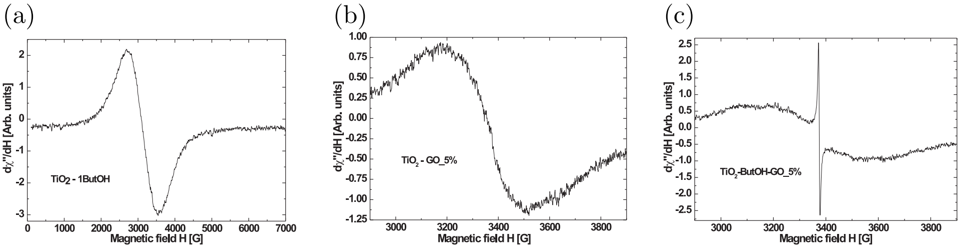

Figure 2. Magnetic resonance spectra at 290 K for: (a) TiO$_2$-1ButOH, (b) TiO$_2$-GO_5% and (c) TiO$_2$-1ButOH-GO_5%

Table 1. g_{eff} parameters for modified TiO$_2$ nanocomposites at liquid helium temperature

Nanocomposites	g_1	g_2	g_3	g_4	g_5	g_6	g_7
TiO$_2$-1ButOH	2.144	2.096	1.983	1.973	1.960	1.928	1.874
TiO$_2$-GO_5%	2.144	2.096			1.945	1.910	1.871
TiO$_2$-1ButOH-GO_5%	2.144	2.096				1.926	1.872

Table 2. g_{eff}, linewidth, ratio integrated intensities parameters for modified TiO$_2$ nanocomposites at room temperature

Nanocomposites	g_{eff}	ΔH_{pp} [G]	I/I_1
TiO$_2$-1ButOH	2.184	854	1.0
TiO$_2$-GO_5%	2.001	331	1.9
TiO$_2$-1ButOH-GO_5%	2.001	425	1.5

This magnetic resonance spectrum is characteristic for magnetic agglomerates. A similar spectrum was observed in the modified titanium dioxide, however, the integrated intensity was lower [2]. Low temperature treatment of the prepared modified titanium dioxide could result in formation of a magnetic agglomeration [3, 4].

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Polymer macromolecules with complex architectures – simulations with parallel FPGA-based dedicated analyzer

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In this work simulation studies of polymer systems containing brushes, bottlebrushes and polymer stars are presented in the frame of their segmental dynamics and solvent dynamics in the direct proximity to polymer chains. This type of simulation is pretty challenging as it must involve a variety of time scales and a broad range of sizes – from small-molecules with Fickian-like dynamics to a segmental motion of chains. An efficient simulation method called the Dynamic Lattice Liquid (DLL) model [1, 2] was proposed by Tadeusz Pakula. This model considers a liquid molecular system as an assembly of structureless beads representing atoms, groups of atoms or polymer segments. The model is based on the assumption that the diffusion steps are realized as a cooperative motion, even for a completely occupied space. The introduction of bonds between beads, representing polymer chains with a complex topology leads to movement constraints connected with the bond stiffness and excluded volume. The DLL nicely represents the dynamics of the whole system, naturally taking into account the diffusive constrains related to polymer chains and crosslinking points. Despite the advantages of the DLL model it is computationally demanding for long polymer chains. This was the reason for the need to use the ARUZ – Analyzer of Real Complex Systems [3]. ARUZ is based on almost 26000 FPGA (Field Programmable Gate Array) devices working as signal processing units and connected in a three-dimensional network. ARUZ is a scalable, fully parallel data processing system equipped with low-latency communication channels, dedicated for simulations involving interactions among a huge number of relatively simple elements working in parallel. The presented simulations required over 10^9 simulation steps to equilibrate (with the box size close to 1.5 million of elements), and this would take over 300 days on a PC-class computer *vs.* <3 days on ARUZ.

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Calculation of thermal conductivity by Green-Kubo formula using minimum image method

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Thermal conductivity is one of transport coefficients [1] the knowledge of which is important both from the theoretical and practical point of view. The thermal conductivity coefficient can be determined using computer simulations [2]. The Green-Kubo method [3, 4] in Equilibrium Molecular Dynamics (EMD) simulations [2] is one of the most widely used methods. In the present work a method for determining the thermal conductivity by the Green-Kubo formula using the minimum image method (MIM) [5, 6] is proposed and tested on a model system of particles interacting by the Lennard-Jones (LJ) potential [1, 2]. The impact of long-range interactions on the thermal conductivity in a lattice model was considered. When the minimum image method is used, long-range interactions between atoms with the contribution of non-uniform spatial arrangement of particles (concerns crystal symmetry) can be taken into account.

The simulations did not reveal any significant differences between the thermal conductivity values obtained by a method using the MIM and those coming from the classical Green-Kubo approach. It was found that taking into account long-range interactions using the MIM did not affect essentially the calculated thermal conductivity coefficient of the Lennard-Jones crystal. The obtained results are in agreement with the Klemens-Callaway model for thermal conductivity based on the three-phonon Umklapp scattering [7]. The study also shows that size effects in the determination of the thermal conductivity using the Green-Kubo formula with the MIM are negligible.

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ABS16

Preparation, characterization and shape memory properties of poly(butylene terephthalate)/polylactic acid based copolyesters

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Due to the number of advantages such as high tensile strength, sensitivity to hydrolytic degradation and biocompatibility, PLA is one of the most common polyesters for biomedical and pharmaceutical applications. However, PLA is a rigid, brittle polymer with a low heat distortion temperature and exhibits small elongation at break [1, 2, 3]. In order to broaden the range of PLA applications, it is necessary to improve these properties. In recent years a number of new methods have been explored to obtain PLA-based materials with improved characteristics, including manipulation of crystallinity, plasticization, blending with other polymers and incorporation into block copolymers [4].

In the present work, a series of poly(butylene terephthalate)polylactide copolymers (PBT-*b*-PLA) were synthesized and characterized. Materials were prepared by two-step synthesis: transesterification and melt polycondensation. The process was carried out in a polycondensation reactor (Autoclave Engineers, PA, USA) in the presence of catalysts: $Zn(CH_3COO)_2$, Sb_2O_3 and thermal stabilizer - IRGANOX 1010.

A set of ^{1}H NMR and ATR-FTIR investigations confirmed unambiguously that the lactide moieties were successfully incorporated into the PBT backbone. The applied method promotes the organization of T, BG, and LA units in blocks of different lengths, as detected by the ^{1}H NMR sequence analysis. The average weight ($\overline{M_\mathrm{n}}$) number of synthesized copolyesters ranged from 32 156 to 26 488 g/mol. Although the PBT-*b*-PLA copolyesters were found to be miscible in the amorphous phase, the phase separation arising from PBT crystalline domains occurred. Along with an increase in the PLA weight fraction in copolymers, the length of aromatic sequences decreased which in turn resulted in shifting the values of melting temperatures (Tm) toward lower figures and lowering the crystallinity degree ($\mathrm{x_c}$). Copolymerization with PLA significantly affected the mechanical performance, providing high elongation but reducing Young's modulus, yield strength, and strength at break at the same time.

Although incorporation of PLA leads to a drop in the thermal stability, all copolymers remained stable up to a temperature as high as 356°C.

Additionally, the PBT-*b*-PLA 30 copolymer exhibits a range of attractive features including the low glass transition temperature of $\sim 35°$C, an amorphous structure (with the ability to develop morphology by isothermal crystallization), the ability to elongate substantially as much as $\sim 285\%$ and finally shape the memory properties. It was found that the mechanism of its shape memory behavior benefited from the glass transition temperature. The PBT-*b*-PLA 30 copolymer showed a satisfactory shape-fixity ($\geq 91\%$) and a shape recovery efficiency ($\geq 94\%$) that remained reproducible over multiple shape memory cycles. It is believed that these properties make the PBT-*b*-PLA copolymer a suitable candidate for biomedical applications.

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Structural and magnetic properties of one-pot solvothermal synthesized graphene/25% $ZnFe_2O_4$ composites

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Nanocomposites containing graphene and $ZnFe_2O_4$ were synthesized and characterized. The structural and magnetic properties of the composites were determined. The content of zinc ferrite in the composites was 25 wt.%. The materials were obtained using two pressure methods: synthesis in the autoclave and synthesis in the microwave solvothermal reactor. The phase composition was systematically investigated by X-ray diffraction (XRD). The structural properties were investigated using low temperature nitrogen adsorption, density measurements and TG measurements. The morphology and the structure of the obtained samples were characterized using transmission electron microscopy (TEM). The properties of the composites obtained using both methods were compared. The magnetic properties were investigated by the magnetic resonance method. The magnetic resonance lines were fitted either by using the composition of Lorentzian and Gaussian functions or only by Lorentzian functions. All spectroscopic parameters strongly depended on the annealing temperature and the applied stress.

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Technology of real-world analyzers (TAUR)

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The article describes the most important project assumptions for a reconfigurable construction of dedicated electronic machines intended for performing analyzes of phenomena occurring in multi-component systems containing at least several million of mutually interacting elements. Devices built in the presented technology are characterized by: the use of reconfigurable integrated circuits, a spatial structure ensuring scalability, a redundant panel system, as well as specially developed data transmission and supervision control systems. Machines work in a parallel manner solving problems in various fields of science and technology and are alternative for supercomputing systems with a high speed of data processing for parallel algorithms. The ARUZ system, containing 26,000 FPGAs, made using this technology is briefly presented as an example.

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Characteristics of wustite based iron-cobalt catalysts for ammonia synthesis reaction

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Wustite is a non-stoichiometric form of iron (II) oxide that is used as a precursor of an iron catalyst in the reaction of ammonia synthesis. The catalyst obtained as a result of wustite reduction has higher activity than the traditional catalyst obtained in the reduction of magnetite.

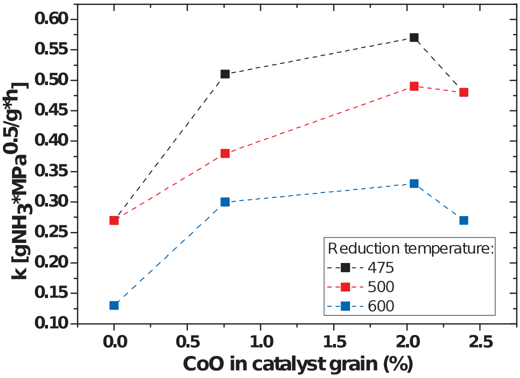

Figure 1. Dependence of catalyst activity on cobalt oxide concentration in catalyst grain at temperature 400°C

The purpose of this work was to determine the effect of the addition of cobalt into an iron-based wustite catalyst structure on the distribution of promoters in precursors, correlation of the activity of these catalysts in the reaction of the ammonia synthesis with hydrogen adsorption on the active surface.

The activity in the ammonia synthesis reaction was tested at 10MPa in the temperature range from 350°C to 500°C.

The promotion with cobalt oxide increased the thermal resistance of the catalysts and significantly increased the activity in the ammonia synthesis reaction.

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Graphitic carbon nitride as highly efficient photocatalyst for dye decomposition in water

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Efficient utilization of solar energy is a frontier research field in the 21st century with intense competition in various countries. Accordingly, photocatalytic processes are a very attractive approach used for the solar energy utilization. Photocatalysis has been regarded as a promising strategy for removing toxic organic and inorganic contaminants in air and water solutions and photocatalytic water splitting into hydrogen and oxygen. It is graphitic carbon nitride (g-C_3N_4) that has attracted the attention of many researchers among the photocatalysts used, due to its unique physicochemical properties such as non-toxicity, high chemical and thermal stability and a narrow band gap (~ 2.7 eV). Unfortunately, bulk g-C_3N_4 has a few disadvantages, which strongly limit any large-scale application. These are (i) a narrow scope of solar energy utilization, (ii) a fast recombination of photogenerated carriers and (iii) a small surface area. Thus, in order to resolve the above mentioned restrictions of g-C_3N_4, researchers are working to construct hybrids which would allow receiving the desirable features of the material. The polymeric nature of carbon nitride allows surface engineering and modification on a molecular level.

Here, the synthesis and description of high active photocatalysts based on graphitic carbon nitride are presented. Bulk g-C_3N_4, exfoliated g-C_3N_4 and composite photocatalysts based on g-C_3N_4 were produced and fully characterized. The physicochemical properties of the obtained materials were investigated via atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and diffuse reflectance UV-vis spectroscopy. Finally, the photocatalytic performance of the obtained samples with regard to the bulk g-C_3N_4 was investigated in the reaction of organic dye (Adid Red 18 and Rhodamine B) decomposition in water under simulated solar light irradiation.

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Multifunctional liquid crystalline chromophores for 3D data storage

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Current optical data storage techniques have fundamental limitations in the available memory density owing to their 2-D nature. To meet the challenges of the big data volume, 3D optical data storage methods are proposed as a way to circumvent this issue by coding the information throughout the volume of the medium. However, to do so, specific voxels (volumetric pixels) only should be addressed by light. One of the most promising approaches for this purpose lies in the application of two-photon absorption (TPA), so that a specific volume can be spatially targeted providing a 3D resolution. Thus, to be able to store massive quantities of information in three dimensional supports, the design of light responsive bulk non-linearly active supramolecular materials is crucial.

A new class of NLO-phores of a D2d symmetry based on a donor-substituted styryl bipyrimidine core with a large TPA cross-section has recently emerged [1]. Bipyrimidine derivatives appear particularly interesting in the design of new NLO-phores because they can easily be functionalized on the styryl fragments to control their hyperpolarizabilities but also by reason of their supramolecular self-assembly abilities in a solution and in the solid state such as in liquid crystalline materials. Liquid crystals are attractive stimuli-responsive matrixes indeed, allowing the preparation of well-organized, anisotropic, soft and malleable thin films.

We demonstrated that applying a rational design strategy, unprecedented chiral and flexible organic liquid crystalline thin films displaying TPA properties could be obtained. Moreover, they would present a strong 2nd harmonic generation (SHG), competitive to inorganic crystalline materials such as KH2PO4 (KDP) [2, 3]. These liquid crystalline phases are stable at room temperature and can be reversibly melted into the isotropic phase around 90°C. For this purpose, chiral carbon chains were grafted on specific positions at the periphery of the bipyrimidine NLO-phore to provide a noncentrosymmetric molecular organization inside thin films.

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Borate-bismuth glasses doped with Ag nanoparticles as a promising hybrid structure for LED application

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Nowadays keen interest is shown in optical materials which, due to their properties, could be used, for example, as non-linear photonic materials, optical waveguides or LEDs. Such materials should have a high refractive index, good transparency in a wide range of frequencies, high thermal stability and a desirable mechanical stability as well as low phonon energy. Borate-bismuth glasses and glass-ceramics doped with Ag nanoparticles can be proposed as novel materials for such applications.

In this work the results of the investigation of structural and optical properties of B_2O_3-Bi_2O_3 or B_2O_3-Bi_2O_3-BaO glasses and glass-ceramics, doped with Ag nanoparticles and Eu^{3+} ions are presented. The glasses were prepared by a conventional melt-quenching method. Ag nanoparticles were grown during thermal annealing. Such a method for the nanoparticle preparation in a glassy matrix was successfully employed, *e.g.* in tellurium glasses [1]. The structure of the samples was studied by XRD, DSC and FTIR methods, while the optical properties were examined by UV-Vis spectroscopy. In addition, the luminescent properties of $^{3+}$ ions under excitation by UV light were investigated.

Based on the tests carried out, it can be said that the proposed borate-bismuth glasses and glass-ceramics are a very promising material, as a host material for LED diodes.

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Structure and synthesis of thin TiO_2 films with Au nanoparticles for photovoltaic applications

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For several years now, since the limitations in the stability of silicon-based photovoltaic devices were recognized, titanium dioxide has dominated photovoltaic solar energy converters. TiO_2 has turned out to be a distinguishing candidate due to its great optical and chemical stability, low cost and nontoxicity. Nevertheless, despite its exceptional properties, solar cells based only on titanium dioxide do not reach satisfying efficiencies for today's reality. Hence, much attention has been paid to novel solutions in hybrid solar cells, where nanoscience plays a greater role [1, 2].

Here, we present a synthesis and optical properties of thin titanium dioxide films enriched with Au plasmonic nanoparticles in four different configurations: plasmonic platforms on and under titanium dioxide thin film fabricated together and separately. The structure and surface morphology of the synthesized systems were investigated by means of XRD and SEM, while the optical parameters were analyzed using UV-Vis spectroscopy. The results show significant enhancement in the absorption bands, which is promising for further photovoltaic applications.

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An advanced approach for fabricating a coral-like nanostructure based on the GaAs substrate for photovoltaic applications

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A large area surface microstructure is commonly employed to suppress the light reflection and enhance the light absorption in silicon photovoltaic devices, photodetectors, and image sensors. However, there have been no simple means to control the surface roughness of III-V semiconductors by chemical processes to date. Here, we propose an advanced approach of etching GaAs wafers for photovoltaic applications. By using the RIE method, we get black GaAs with a coral-like pattern. The coral-like GaAs nanostructure has shown a supreme light trapping property. In the whole range of the visible band, the coral-like GaAs nanostructure effectively reduces the reflectivity of light, so that it remains below 3%. The reflectance of the coral-like GaAs nanostructure is reduced by over 50 times compared to polished GaAs wafers, nearly doubling its absorption. Moreover, we propose a qualitative reaction mechanism by studying the dependence of this process on different crystal orientations. This method provides a new simple and scalable way for improving the light absorption and the power conversion efficiency of GaAs photovoltaic devices.

Relation between structure and surface tension in binary metallic melts

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Detailed information on the structure and physical properties in the liquid state is needed to obtain new alloys with advanced properties. It is especially important at many technological processes to have the relation between the structure and surface tension for binary and more complex alloys.

In this work we compared the results on the temperature and concentration dependences of the structure parameters in Ga-Sn liquid alloys with similar dependences of the surface tension. Unfortunately there are problems with predicting the structure and surface tension at different temperatures and concentrations with the existing theoretical approaches. In addition, the relation between structure parameters and surface tension is developed for simple liquids only, such as liquefied inert gases and monovalent liquid metals. For this reason, the experimental studies of the temperature and concentration dependences of the structure parameters compared with the measured physical properties are of great importance.

The results of our X-ray diffraction and surface tension studies of Ga-Sn liquid alloys showed a deviation from ideal behavior and no absolute correlation between such deviations for structure parameters and the surface tension coefficient was noted. We supposed that such behavior was caused first of all by different concentration of the constituent components in the surface layer and the melt bulk.

Modified carbon spheres as sorbents for CO_2 and CH_4

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Carbon materials such as powders, foams, fibers, nanotubes and spheres are fascinating with their high surface area, high porosity and many extraordinary qualities such as chemical and physical resistance or good electrical properties. Sorption of impurities from gas and liquid phases should be mentioned as possible applications. Furthermore, carbon materials can be easily modified to maximize the efficiency. The subject of the lecture are applications of carbon spheres modified with titania for the adsorption of two greenhouse gases: carbon dioxide and methane. The emission of greenhouse gases is one of the crucial factors influencing climate changes and global warming. Both carbon dioxide and methane are among the most abundant greenhouse gases and a significant and continuous increase in their concentration in the atmosphere can be observed. Then, a decrease in the emission of these gases to the atmosphere has recently become one of the global challenges. There are many solutions proposed to solve the problem, however, in all cases a sorption of gases in a solid or liquid medium has to be carried out as the first step. Our proposition is to apply photocatalysis for transformation of methane and carbon dioxide into useful products. In the paper a candidate for a photocatalyst is presented, based on the composite of titania with carbon spheres. The material was obtained using microwave assisted solvothermal synthesis, enabling a good dispersion of titania. The studies of the carbon dioxide and methane adsorption were performed under ambient pressure and temperatures of 40, 60 and 80°C. The satisfying values of carbon dioxide and methane uptake were reached – 3.94 mmol CO_2/g and 2.77 mmol CH_4/g at 40°C, respectively.

Acknowledgements

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Auxetic properties of f.c.c. hard sphere model with [001]-monolayer inclusions at different pressures

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Elastic properties of models composed of spheres interacting through a hard potential were determined by Monte Carlo simulations using the Parrinello-Rahman method [1–3]. The model consisted of hard spheres σ in diameter that (at close packing and without inclusions) form a perfect f.c.c. lattice. A periodic stack of *nanolinclusions* in the form of monolayers, oriented orthogonally in the [001] direction was introduced into such a system. Particles forming inclusions differ from particles forming the bulk of the system only in the value of their diameters, $\sigma' \neq \sigma$. The hard sphere (purely geometrical) interactions were used for all the particles in the system. Elastic properties, including Poisson's ratio (PR) [4], of such a model have been previously determined for the pressure $p = 100$ [5]. It has been shown that Poisson's ratio of a tetragonal system with inclusions with $\sigma'/\sigma \neq 1$ typically increases along with an increase in the σ'/σ ratio. However, directions can be found (*e.g.* [101][$\bar{1}$01]) for which an increase in σ'/σ causes a decrease in Poisson's ratio from -0.059 down to -0.11 (at $\sigma'/\sigma = 1.054$), thus, enhancement of the auxetic properties [6] was observed.

The purpose of this study was to investigate the influence of pressure (*i.e.* the second parameter characterizing the system) on the elastic properties and Poisson's ratio of the studied system. The system was studied at pressures between $p^* = p\sigma^3/(k_\mathrm{B}T) = 11,\ldots,1250$. It was shown that PR in the direction [101][$\bar{1}$01] at smaller values of σ'/σ could be decreased by increasing the pressure. The observed Poisson's ratio in this direction was as low as -0.18 at $\sigma'/\sigma = 1.05$ for $p^* = 250$.

The results of this study show that PR of nanocomposites at high pressures can be efficiently modified by slightly changing the sizes of selected particles (those forming the nanoinclusions).

Acknowledgements
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Chemical short range ordering in liquid intermetallics

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The structure of liquid intermetallics is significantly different from the structure of simple metallic melts which are commonly described by means of ideal or regular solution models. The current growth of interest in intermetallics is primary caused by their unique properties, which can be improved by an addition of other elements or thermal treatment. One of the fruitful methods is treatment in the liquid state, which unfortunately is used less frequently in comparison with traditional thermal treatment methods. For this reason, it is of large importance to study the structure and properties of liquid intermetallics as well as their temperature dependences.

In this work we present the results of structure studies of liquid binary compounds, existing in a Ni-In binary system. X-ray diffraction patterns were obtained at different temperatures using a high temperature X-ray diffractometer. A sample was placed in a vacuum chamber, filled with pure helium to avoid oxidation. Experimental data was used to calculate the structure factors and pair correlation functions, from which the main structure parameters were calculated. Using the experimental data and the existing models of the liquid metal structure allowed us to describe the main features of the chemical ordering and behavior of such ordering with temperature and composition variation.

Tunnelling effects of a Gaussian wave packet impinging on a barrier

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A general procedure based on momentum-like quantity provides the reflection and transmission amplitudes for a given barrier sandwiched by semiconductor reservoirs is presented. Furthermore, the evolution of the wave function stemming from an initial Gaussian wave packet located on the left hand side of the barrier with ignorable barrier overlap is obtained. The evolving wave function enables obtaining the associated probability and current densities space and time-wise. As application the cases of smooth double, and quadruple barrier are considered. The numerical results exhibit the picture obtained via propagator, in the limited cases of square and double square barrier, *e.g.* repeated current density reversal at the barrier entrance, while being unidirectional at the exit. Presently, the treatment takes account of any barrier, inclusive of applied voltage, and transverse magnetic field. The basic quantity required is the value of the momentum-like quantity at the barrier entrance, which is obtained solving a Riccati equation governing the quantity, in question, whose value is known at the barrier exit in terms of the carrier energy and applied bias.

ABS30

A comparison study on the phase structure and functional properties of PTF-block-PTMOF and PTF-block-PCLF copolymers

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Over the last century, the world has become increasingly dependent on oil as its main source of chemicals and energy. Driven largely by the strong economic growth of India and China, the demand for oil is expected to increase significantly in the coming years. This growth in demand, combined with the diminishing reserves, will require the development of new, sustainable sources for fuels and bulk chemicals. Biomass is the most attractive alternative feedstock, as it is the only widely available carbon source apart from oil and coal.

Nowadays, academic and industrial research in the field of polymer materials is strongly oriented towards bio-based alternatives to petroleum-derived plastics with enhanced properties for advanced applications. In this context, 2,5-furandicarboxylic acid (FDCA), a biomass-based chemical product derived from lignocellulose, is one of the most high-potential biobased building blocks for polymers [1] and the first candidate to replace the petro-derived terephthalic acid. The aim of this study was to compare the functional properties resulting from the phase structure of the novel multiblock copolymers based on poly(trimethylene furanoate) (PTF) as a rigid segment and a flexible polyether segment (PTMO) or polycaprolactone (PCL) (Figure 1). The influence of the amount of PTMO and PCL on the structure as well as the mechanical and thermal properties of the obtained block copolymers were investigated.

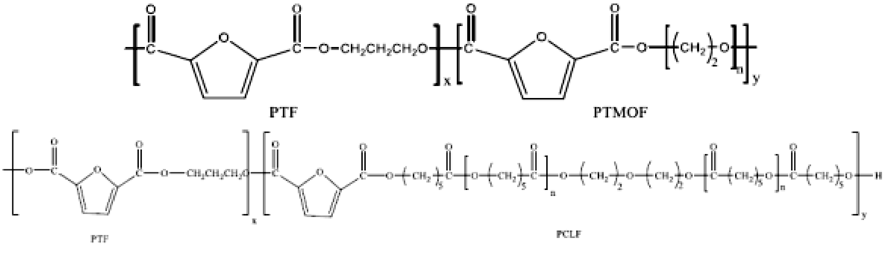

Figure 1. Chemical structure of PTF-block-PEOF and PTF-block-PCLF copolymers

ABS30

PTF-*block*-PTMOF and PTF-block-PCLF copolymers were synthesized by means of a two-step polycondensation process [2,3] by using 2,5- dimethylacetylenedicarboxylate (DMFDCA, China), bio-1,3-propanediol (DuPont Tate & Lyle BioProducts, USA), α,ω-techelic polycaprolactone (PCL) diol with the molecular weight of 1250 g/mol (Polysciences Europe, Germany) and bio poly(tetramethylene oxide) with the molecular weight of 1000 g/mol (PolyTHF, BASF, Germany), a thermal stabilizer (Irganox 1010. Ciba Geigy, Switzerland) and tetrabuthyl orthotitanate (Sigma-Aldrich) as a catalyst. Along with the DSC and DMTA methods the supramolecular structure of block copolymers was studied, whereas the functional properties were tested during tensile and thermogravimetry measurements.

The synthesized materials exhibited a heterophase structure. It can be also found that the tensile properties of the copolymers were strongly affected by the number of the flexible segments of PEOF or aliphatic polyester (PCLF). Moreover, along with an increase in the PEOF or PCLF content a decrease in the thermo-oxidative stability was observed.

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Preparation method of nanocrystalline iron oxides with various average crystallite size and investigated by magnetic resonance method

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A series of nanocrystalline iron oxides differing from each other in the average crystallite size (26 to 37 nm) were prepared.

The raw material for the prepared samples was nanocrystalline iron with the average crystallite size of 21 nm (sample M0) which was obtained by fusing magnetite with small amounts of promoters such as Al_2O_3, CaO, K_2O (max. 10% in total), followed by the reduction of the oxidized alloy with hydrogen at the temperature of 500°C. Finally, the sample was passivated in order to avoid autoignition.

Samples of nanocrystalline iron oxides were obtained by the following steps:

1 g of passivated nanocrystaliine iron was placed in the platinum basket in the form of a single layer of grains inside a tubular differential reactor with thermogravimetric (TG) measurement. The passive film was reduced polythermally with hydrogen (12 dm^3 $H_2/(h\ g)$), increasing the process temperature from 20 to 500°C. Then, the atmosphere inside the reactor was changed from reducing (hydrogen) to inert (nitrogen). The next step was oxidation of nanocrystalline iron with water vapor in a stream of nitrogen (0.02 bar H_2O). The oxidation was performed until different oxidation degrees (related to magnetite) were obtained. The oxidation process was conducted under conditions where the process rate was limited by the surface chemical reaction rate. Iron nanocrystallites underwent phase transition to magnetite in the order from the smallest to the largest size. It means that with an increase in the conversion degree, the average crystallite size of the new phase also increased. The magnetite content expressed by the mass fraction varied from 0.16 for sample M1 to 0.60 for sample M5 – determined by means of the TG method. After oxidation, the process samples were cooled down and passivated. The phase composition as well as the mean size of nanocrystallites were determined by using the X-ray diffraction method. The average crystallite size of particular samples was 26, 29, 32, 35 and 37 nm for samples M1, M2, M3, M4 and M5, respectively. Non-oxidized iron in the samples was etched with dilute nitric acid (V) what resulted in obtaining a series of

samples with the composition close to 100% of magnetite and different mean crystallite sizes. The magnetic resonance spectra were investigated and are presented in Figure 1. Sample M0 does not have intense resonance spectra. The recorded magnetic resonance spectra are similar to those for Fe_3O_4 [1] and were fitted by Lorentzian and Gaussian functions. All the magnetic resonance parameters depend on the way of preparation of samples. Figure 2 presents differences of the position of resonance lines depending on the concentration of Fe_3O_4. Greater differences were observed for the nanocomposite with the nanocrystallite size of 35 nm. A weak anisotropy was observed for smaller concentrations. Figure 3 shows the dependence of the total integrated intensity on the size of nanocrystallites. Intensities increase as well with an increase in the size of nanocrystallites.

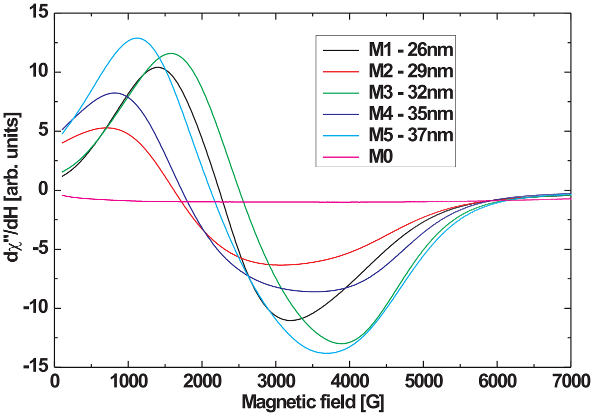

Figure 1. Magnetic resonance spectra

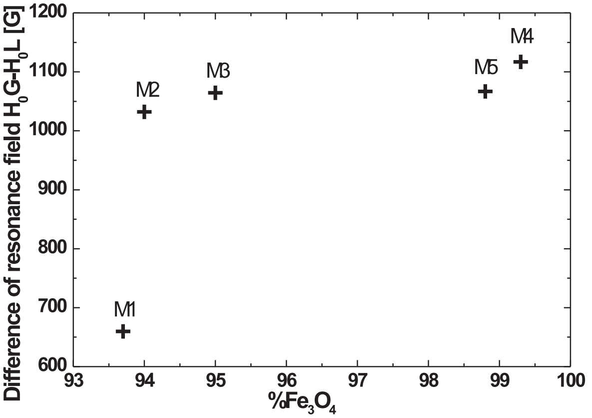

Figure 2. Difference of resonance field

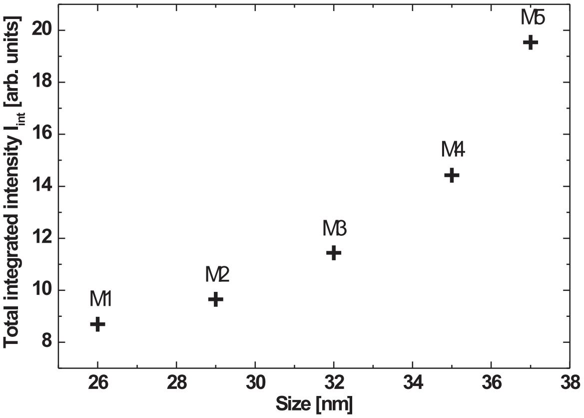

Figure 3. Total integrated intensity

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Nanocrystalline iron nitride γ'-Fe_4N with various average crystallite size and magnetic resonance spectra

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A series of nanocrystalline iron nitrides γ'-Fe_4N with various average crystallite sizes ranging from 23 to 52 nm were obtained.

The raw material for the reference sample was nanocrystalline iron promoted with small amounts of metal oxides (Al_2O_3, CaO, K_2O) and with the average crystallite size of 21 nm which was prepared according to the method described in Ref. [1].

Nanocrystalline iron was subjected to a nitriding process in order to obtain γ'-Fe_4N. For this purpose, at first a passive layer on the surface of nanocrystalline iron was reduced at hydrogen in 500°C. After the reduction, the temperature inside the reactor was reduced to 350°C and the sample was nitrided isothermally at this temperature under atmospheric pressure, in a stream of an ammonia-hydrogen mixture. The nitriding potential of the NH_3-H_2 mixture can be described by the following equation:

$$P = \frac{p_{\mathrm{NH}_3}}{p_{H_2}^{3/2}}$$

where P is the nitriding potential [$\mathrm{Pa}^{-1/2}$] and p_x is partial pressure of components [Pa].

The process of nitriding was carried out with the nitriding potential $\ln P = -4.8$ until the weight of the sample was stabilized. Then the sample was cooled down in a stream of nitriding mixture and next passivated. In this way a reference sample (N0) of iron nitride γ'-Fe_4N with crystallite size equal to 23 nm was obtained.

In order to obtain samples from N1 to N4 the raw iron material was subjected to a series of processes such as oxidation with water vapor and etching with diluted inorganic acid described in more detail in [1]. In the next step the magnetite that remained in the samples after etching was reduced with hydrogen and then the samples were nitrided under the same conditions as the N0 sample. In this way iron nitrides γ'-Fe_4N with the average nanocrystallite size equal to 35, 42, 48 and 52 nm were obtained for samples N1, N2, N3 and N4, respectively.

Figure 1 presents the magnetic resonance spectra for the investigated nanocomposites. These spectra are mostly as intense, very broad and asymmetrical as in [2]. The spectra were deconvoluted using the Dyson function in four components. All parameters of the magnetic resonance spectra are different when compared to those obtained in [2]. Figure 2 shows the positions of the resonance lines. These positions of the resonance lines strongly depend on the internal magnetic fields. They are forming different systems of correlated spin magnetic agglomerates. Figure 3 presents the total integrated intensities which are changing significantly. Probably it is connected with the sizes of the magnetic agglomerates.

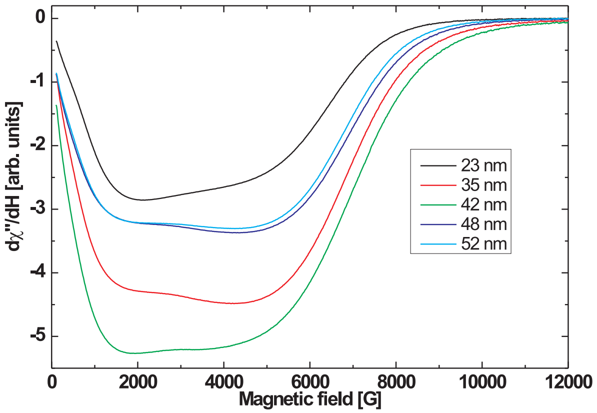

Figure 1. Magnetic resonance spectra

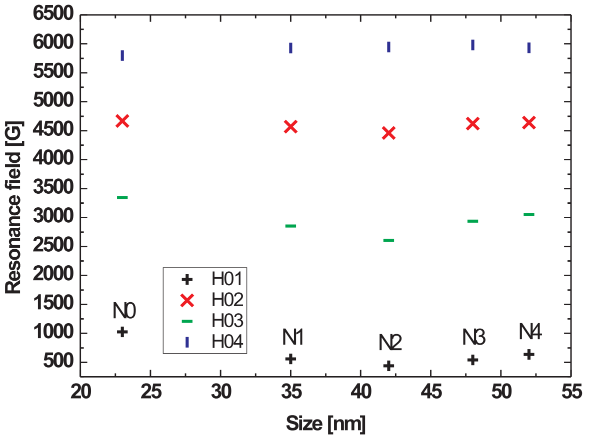

Figure 2. Difference of resonance field

Acknowledgements

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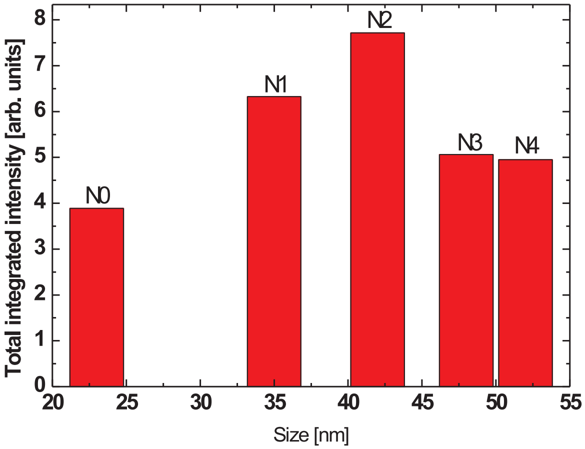

Figure 3. Total integrated intensity

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Chemical equilibrium of catalytic nanomaterials

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According to a common opinion, materials consisting of nanometer-sized crystallites are far from thermodynamic equilibrium. However, despite prolonged exposure to high temperatures, neither the surface area nor the metal dispersion of metal catalysts reach zero and the catalysts maintain their properties under reaction conditions. For example, the iron ammonia synthesis catalyst, *viz.* nanocrystalline iron promoted with aluminum, calcium and potassium oxides preserves its unchanged developed structure for 12 years of operation. Studies concerning the impact of the temperature and the chemical composition of the catalyst on its properties were conducted to confirm the hypothesis that the structurally promoted materials with a highly developed specific surface area were in a state of chemical equilibrium [1]. In a double-layer model of the catalyst surface [2] it was proposed that the specific surface area of the catalyst was proportional to the amount of oxygen adsorbed on that surface. The surface energy is compensated by the energy of bonds created between the surface metal atoms and the structural promoter oxides, hence, the existence of the equilibrium state is possible. Albeit, there has been no thermodynamic data describing such systems.

A two component model system in which the surface of a single crystallite of substance A was covered with additional substance B with a specified degree was studied. In the model system, nanocrystalline material was prepared at a high temperature, at which diffusion did not limit the mass transport. The obtained structure resulted from the balance between the surface and the volume of crystallites and their surroundings in isothermal-adiabatic conditions. The surface of a single crystallite was then covered with an additional substance with a specified degree. Energy had to be added to the system to develop a solid surface [3]. That energy can be delivered during such processes as adsorption or segregation while the substance concentration on a solid surface changes. In isothermal-adiabatic systems, changes of a specific surface area are a function of the following parameters:

$$\frac{S_1}{S_0} = f(\theta, \gamma, Q)$$

S_0 – uncovered surface, S_1 – covered, enhanced surface, θ – coverage degree, γ – surface energy, Q – heat of interactions between surface atoms of substance A and substance B.

Model calculations were carried out on the basis of the elaborated equations describing the effect of the temperature on the value of the surface coverage degree, and consequently on the surface development degree. Based on the energy-balance calculations it was concluded that the reduction in the surface area was associated with a decrease in the surface coverage degree and thus with the need to provide energy to the system to remove the chemisorbed atoms (Figure 1). An increase in the temperature of a nanocrystalline substance to a temperature higher than the preparation temperature results in the formation of a new state of equilibrium defined by larger sizes and a lower number of crystallites, and hence, by a smaller specific surface area. In practice, lowering the temperature does not change the size and the number of crystallites due to the low rate of this process, although an increase in the fineness degree is thermodynamically possible. A system reaches the equilibrium state at a temperature equal to or greater than the temperature at which it was obtained. At temperatures below the maximum temperature, the issues that can be discusses are only the balance between the gas phase and the surface the structure of which may change through the faceting processes due to diffusion of surface atoms.

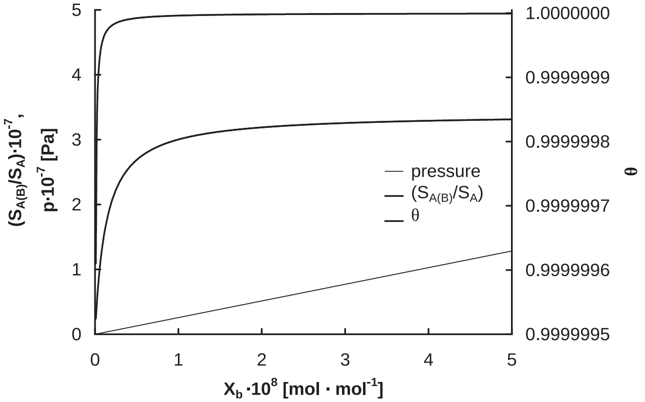

Figure 1. Surface development degree ($S_{\mathrm{A(B)}}/S_{\mathrm{A}}$), surface coverage degree (θ) and pressure (p) of substance B in gas phase as function of bulk concentration of substance B (x_{B}). Calculation data: $\Delta G_{\mathrm{seg}} = -180\,\mathrm{kJ\cdot mol^{-1}}$, $T = 573\,\mathrm{K}$, $K = 100$, $\gamma_{\mathrm{A}} = 170\,\mathrm{kJ\cdot mol^{-1}}$, $\gamma_{\mathrm{A(B)}} = 10\,\mathrm{kJ\cdot mol^{-1}}$.

Changes in the specific surface area along with changes in the coverage degree present the equilibrium states. The model results obtained in the above considerations are in very good agreement with the double layer model assuming the existence of the equilibrium state of an iron ammonia synthesis catalyst and also with the experimental results [1, 4]. The results shed new light on the structure of nanomaterials. Under certain conditions, the stable structure of these materials is a result of maintaining a state of thermodynamic equilibrium.

Acknowledgements

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Poly(butylene terephthalate)/polylactic acid based copolyesters and blends: miscibility-structure-property relationship

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Owing to their excellent thermal and mechanical properties aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and poly(trimethylene terephthalate) (PTT) have been widely applied in the packaging or textile industries and as engineering materials [1, 2]. Unfortunately, aromatic polyesters are highly resistant to degradation and remain stable over a long period of time, which is often an undesirable feature, in particular for short-term applications [3]. On the other hand, biodegradable aliphatic polyesters are generally characterized by poor thermal and mechanical performance [1, 4]. In this respect, the preparation of aliphatic-aromatic copolymers or physical blends of aliphatic and aromatic polymers have been attracting considerable attention as they may combine the mechanical performance of aromatic polyesters with the biodegradability known from aliphatic polymers.

In this work, aromatic-aliphatic PBT-*b*-PLA copolymers were prepared by reactive melt blending, *i.e.*, the introduction of PLA in a PBT polycondensate followed by a conventional polycondensation reaction. The obtained copolymers were further compared to PBT and PLA homopolymers and the PBT/PLA physical blends prepared simply by the extrusion process.

By applying different methods of preparation, *i.e.*, physical and reactive blending, two systems with significantly differing properties were obtained. The PBT and PLA are immiscible in the molten state and appeared as phase separated systems when prepared by extrusion. It was found that physical blending with PLA accelerated PBT crystallization when cooling from the melt and promoted the cold crystallization of the PLA. As expected, a high crystallinity degree and poor miscibility in PBT/PLA physical blends resulted in the brittle fracture behavior. Although the calculations based on theoretical group contribution methods suggested immiscibility of PBT and PLA, it was assumed that the compatibility in reactive blends increased as a result of chemical bonding between the functional groups of PBT and PLA (ester linkages).

On the basis of two different experimental approaches (DSC and DMTA studies), it was affirmed that only one amorphous phase was formed in copolymer systems. Nevertheless, the micro-phase separation was found to develop owing to the presence of crystallizing PBT blocks. The thermal and structural properties strongly depend on the aromatic block length. It was observed that the degree of crystallinity and the melting temperature decreased along with the decreasing PBT block length (increment of the PLA content) in a copolymer. This means that the crystallinity in copolymers can be controlled by controlling the PBT to PLA ratio. Copolymerization with PLA significantly affected the mechanical performance, providing high elongation but at the same time reducing Young's modulus, yield strength, and strength at break. Incorporation of PLA leads to a drop in the thermal stability of both copolymers and blends with respect to PBT.

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Molecular dynamics simulations of interlayer structure between Au thin film and Si-substrate

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Investigations of material properties on the nanometric scale have always been a major topic of scientific discussion both from the fundamental and industrial points of view. The properties of materials on this scale become sensitive not only to the size of the investigated sample, but also to the shape and composition of the atomic clusters or the precipitates present therein. To achieve meaningful industrial applications of systems composed of nanoparticles, investigation of atomic motions is needed to understand the main mechanisms which occur during the formation of such structures. One of the examples of the importance of this type of investigations are systems composed mainly of gold and silicon. Silicon is a widely used material in semiconductor electronics due to its unique set of properties, which have been observed to be stable over time and over a wide range of temperatures. Likewise, gold is also a common material in this field of industry, being used during production of interconnects found in the most advanced electronic devices. However, due to the miniaturization of such devices, the processes which take place on a scale comparable with the size of a single atom become more and more crucial to the topic of properties exhibited by nanometric Si-Au systems.

Due to the difficulties often encountered when trying to characterize such processes by use of experimental methods, computational methods can be used to explicitly observe atomic motions at the nanometric scale and further our understanding in this topic. One of such methods is the Molecular Dynamics (MD) method, which may allow us in case of Si-Au systems to complement the theory of the formation of gold nanostructures. If such theory can be validated, it can be used to help design and fabricate novel integrated devices and technologies.

During our research, the interaction of gold nanolayers on a substrate composed of a (111) crystal silicon surface was investigated by means of the MD method. In case of the size of those layers, four different thicknesses were considered: 2, 3, 5 and 7 atomic Au layers. The formation of the alloy with a concentration comparable to that found at the eutectic point of Si-Au systems was observed. Such an alloy begins to form mainly on the gold-silicon interphase boundary and plays a crucial role in the dynamics of the investigated systems. It has been shown that the interphase mixing mechanism differs with respect to the temperature at which the simulation of the Si-Au system was carried out. This difference is mainly in the form of the most dominant diffusion mechanism being observed during the mixing of crystalline Si and Au phases.

These conclusions may serve as a part of the theoretical basis applied during the design of the technological processes used for production of electronic devices, mainly from the point of view of their thermodynamical conditions such as temperature. Moreover, the results of our research may further our knowledge of processes occurring at the interphase boundary, which is a very important topic of physical chemistry and which is still tackled by scientists worldwide.

Interactions between nanostructures and a phospholipid bilayer – an MD study

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The cell membrane has been developed as an effective barrier to protect the interior of the cell from the external conditions.

A main, functional part of this barrier is a phospholipid bilayer, a structure consisting of phospholipid and cholesterol molecules. In our model the phospholipid bilayer was indented by various nanostructures such as carbon, silicon-carbide and boron-nitride nanotubes and graphene sheets. In case of the CNTs and graphene sheets various sizes of indenters were used: (8, 8), (10, 10) (12, 12) for CNTs and 5×1 nm and 5×5 nm for graphene sheets. Two indentation speeds were used, 1 and 2 m/s. All simulations were performed in a physiological temperature. The systems were modeled on a fully atomistic level. The SMD technique was utilized to move nanostructures via the membrane. The average force acting on the nanostructure and the work required during the membrane penetration were calculated as a function of indentation depth. The structural changes in the membrane induced by outside objects were also assessed.

Our simulations show that nanoobjects, especially nanotubes, seem to be good candidates to be used as nanocontainers for delivering cargo to cells. They penetrate the membrane quite effectively and the damage caused by the indentation process is limited.

The figure shows a set of snapshots of the nanoindentation process of the bilayer by the (12, 12) nanotube: (a) initial configuration, (b) CNT reaches the polar heads of phospholipids, (c) CNT reaches the glycerol backbone, (d) CNT reaches the second layer of the membrane, (e) final configuration.

Acknowledgements
The calculations were performed at the ICM University of Warsaw, Grant No. G53-6. This research was supported in part by the PAAD Infrastructure co-financed by the Operational Programme Innovative Economy, Objective 2.3.

Mechanical, structural and thermophysical properties of phases found in solid Al-Cu alloys – comparison of selected empirical potentials

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The presentation will start with an overview of a selected group of empirical potentials which are widely used for simulating Al-Cu alloy systems. These potentials were chosen due to their widespread and successful use in various MD simulations. After this introduction, requirements for validating these potentials will be presented *e.g.* their ability to correctly predict the mechanical or thermophysical properties of phases found in the aforementioned alloys. In what follows, a set of computational methods will be outlined, which are used to compute each group of the said properties. These methods include, for example, a simulation scheme used for calculating elastic constants of phases found within Al-Cu alloys or an improved two-phase "sandwich" method used for estimating the melting point of both copper and aluminum. Based on the results of these simulations, each potential will be categorized in terms of the properties for which it predicts values comparable with the available data obtained via experimental and *ab initio* methods.

Rippled graphene and its properties

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We present results of molecular modelling simulations that have been performed on rippled graphene with patterned defects. We show that when defects are positioned in a collinear manner, graphene folds in a manner which results in anomalous mechanical behaviour.

Structure of Ga-Sn composites with NiO nanoparticles

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Currently, the development of light high-tensile and low-cost advanced materials is underway. As a result, many materials have reached their maximum valuable properties. As a consequence, there is a problem of further improvement of properties and creation of new materials, such as multiphase composites. One of the key advantages of such composites, in comparison with traditional materials, is their high durability and stiffness. For many years, a rapid increase in the number of studies on composites based on strong fibers and various polymer matrices has been seen. According to the forecasts, their production will continue to grow, with an increasing relative quantity of composites based on metals and ceramics.

In our work, the main focus is on the study of the effect of disperse particles on the structure of the matrix of a composite in a liquid state. The hypereutectic $Ga_{80}Sn_{20}$ alloy was used in the study. It is promising to be used as a diffusion hardening alloy due to the formation of high-temperature phases by the reaction diffusion with dispersed particles having a high melting point. NiO particles were chosen as disperse particles which can be reduced to pure nickel directly in the melt. The diffusion process at the boundary of the liquid-crystalline phases depends to a large extent on the atomic structure, therefore, the purpose of this work is to establish changes in the structure of a liquid metal matrix under the influence of disperse oxide particles introduced into it.

Therefore, the hypereutectic $Ga_{80}Sn_{20}$ alloy structure in the liquid and solid states and the influence of the disperse particles of nickel oxide on its structure using the X-ray diffraction and electron microscopy methods were investigated. The structure model of this alloy was established. It is assumed that due to the wetting of the surface of nickel oxide particles by the melt on the interface, an increase in the degree of ordering the melt structure and the appearance of atomic groups with a covalent bond type occurs.

Dynamics in complex macromolecular systems

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In general, intracellular and extracellular environments are usually densely crowded and contain different elements such as lipids or proteins [1]. Theoretical studies of dynamics of such systems require special simulation algorithms. We present the applications of the Dynamic Lattice Liquid (DLL) model. Molecule movement in crowded environments was studied by means of extensive Monte Carlo simulations. A two-dimensional coarse-grained model is supposed to mimic a lateral motion of probe molecules in a membrane. The systems studied contained obstacles that were fixed or underwent a Brownian motion; they can also be formed of flexible chains [2]. For this purpose two molecular transport mechanisms were employed: the Single Agent Model where the motion of an object is considered as a random walk without any correlation with other moving elements [3] while the second model of motion was based on the DLL model which was built on the cooperative movement concept [4]. The conditions at which anomalous diffusion appeared in the system were analyzed. The influence of mobility, size and concentration of obstacles on the static and dynamic percolation threshold was shown. The mobility of objects, critical exponents and the shape of molecule trajectories were also studied. A comparison with theoretical predictions was made. The impact of the mechanism of transport on the dynamics of such systems was suggested.

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Influence of compensation defects on spectroscopic properties of phosphors

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Many technological processes require, for proper execution, the presence of functional materials characterized by strictly defined properties. Processes based on catalysis, water splitting technologies and lighting technologies use, inter alia, systems consisting of an inorganic matrix and active centers in many different oxidation states incorporated into the matrix. Owing to the invaluable properties of systems containing active centers in various oxidation states, research and development of such systems is becoming highly desirable. The aforementioned systems are important in lighting technologies because they enable the application of cheap light sources based on white light emitting diodes (WLED) in manufacturing. Basically, a white light source is obtained by physically mixing a few phosphors exhibiting blue, green and red emissions in an appropriate weight ratio. Such a procedure is ineffective and can be replaced by a synthesis of a system consisting of a matrix activated by lanthanide ions in two different oxidation states (*e.g.* Eu^{2+}/Eu^{3+}). From the technical perspective, obtaining such systems requires strict control of the reduction process which usually takes the form of controlling the process duration. However, control of the reduction process duration is quite imprecise as far as obtaining a strictly defined ratio of the two oxidation states of a dopant is concerned.

The most recent research shows that the precise control can be achieved by aliovalent co-doping of a matrix – lanthanide system. These co-dopants can be considered as compensators for the charge of $Ln\_Me^{\bullet}$ defect and, thus, Eu^{3+} stabilizers. Some results concerning the stabilizing conditions of a given oxidation state of lanthanides indicate that the reduction process is related to the elimination of a previously formed compensator of the $Ln\_Me^{\bullet}$ defect, for example, a metal vacancy, from the immediate vicinity of the reduced lanthanide ion. This means that the more stable the compensator, the more stable the Eu^{3+} ion under reductive conditions. The compensation of the charge related to the $Ln\_Me^{\bullet}$ defect can be eliminated either by forming another defect (a secondary compensator) in the vicinity of the primary compensator, which will compensate the remaining negative charge after the reduction, or by physically removing the compensator via its migration in the crystal lattice from the reduced ion to the crystal surface. The introduction of the co-dopants and thus the creation of chemically induced compensating defects can be executed using several strategies. One of the strategies is to introduce into a phosphor matrix ions in an oxidation state which is different from the oxidation state of the matrix ions both in the cationic sublattice (*e.g.* introducing Na^+, Li^+, Rb^+, Y^{3+} ions in the place of Me^{2+} ions) and in the anionic sublattice (*e.g.* introducing Al^{3+}, P^{5+} ions in the place of Si^{4+} ions in silicates or Al^{3+}, Si^{4+} ions in the place of $P5^+$ ions in phosphates). Another strategy is to change the stoichiometric ratio of heterovalent ions in the matrix (*e.g.* changing the [Ca]/[Y] ratio in the $Ca_9Y(PO_4)_7$ matrix).

In this contribution a qualitative explanation of the influence of the compensation defects created via the above mentioned strategies on the spectroscopic properties of europium doped phosphors will be presented.

Acknowledgements
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Selective auxeticity enhancement due to nanochannel structure change in Yukawa crystals

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Particles interacting via the hard-core repulsive Yukawa potential [1] can be used to model various physical properties of colloidal suspensions [2, 3]. Monte Carlo (MC) simulations in an isothermal-isobaric ensemble were performed to evaluate the orientational dependence of Poisson's ratio (PR) of model Yukawa crystals with a periodic array of nanochannels filled by hard spheres and parallel to the [001] crystallographic direction. It is known that PR of a defect free Yukawa crystal is negative in the $[110][1\bar{1}0]$ direction [4]. Moreover, the PR value in this direction can be lowered by increasing the Debye screening length [4]. Recently, it has been shown that the presence of nanochannel arrays, filled by hard spheres in the system causes a decrease in the value of PR in the $[110][1\bar{1}0]$ direction [5]. Apart from that, effects of selective enhancement of auxeticity through changes in nanochannel diameters in Yukawa systems have been observed [6]. In particular, it has been found that depending on the choice of the nanochannel diameter the auxetic properties of the system can be enhanced in one of two selected crystallographic directions ($[110][1\bar{1}0]$ or $[011][01\bar{1}]$) [6].

The present study is devoted to the investigation of the microscopic structure of the studied systems. Some interesting transformations of the crystalline structure near nanochannels are observed.

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ABS43

Influence of reduced Ti^{3+} on the formation of hydroxyl radicals under visible light

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It has been already proved that the presence of reduced Ti^{3+} centers can increase the visible light activity of TiO_2 and also can enhance its photocatalytic properties by retarding the rate of electron/hole pair recombination [1, 2]. Photogenerated electrons upon irradiation can be trapped and tend to reduce Ti^{4+} cations to the Ti^{3+} state. Another process for Ti^{4+} reduction to Ti^{3+} is usually accompanied by a loss of oxygen from the surface of TiO_2. Such surface defects can be formed by annealing TiO_2 in a vacuum condition, thermal treatment under reducing atmosphere (H_2, CO), or by bombardment using an electron beam, neutron, or γ-ray. A formation of titania defects can be also obtained by doping TiO_2 with some anionic species such as N, C, F or others. The way of preparation and temperature of titania reduction has impact on the localization of the trapped charge [3].

In the presented results, the reduced titania was obtained by modification of titania raw material with an ammonia gas under thermal treatment at 300–700°C. Such modification caused nitrogen doping and formation of Ti^{3+} centers above 400°C. XPS and FTIR measurements showed that nitrogen was partly doped to TiO_2 at the interstitial position and partly adsorbed on the TiO_2 surface in the form of ammonia groups. Above 400°C the surface nitrogen groups were desorbed and interstitial doped nitrogen was segregated from bulk to the surface. As a consequence, some of the surface defects in the form of oxygen vacancies and Ti^{3+} centers were formed, what was confirmed by EPR measurements. XRD analyses indicated, that at 700°C , the anatase partly transformed to rutile and the phase composition of TiO_2 consisted of anatase and rutile with the ratio of 75/25, respectively. The EPR analyses showed that the highest amount of Ti^{3+} centers of reduced anatase was formed at 600°C, but at 700°C a reduced form of rutile appeared. The photocatalytic activity of the prepared sample under visible light was tested in the reaction of therephtalic acid conversion. A halogen lamp with a cut off filter of λ¡425 nm was applied as the source of light. 2-hydroxy terephtalic acid as a product reaction of therephtalic acid with hydroxyl radicals formed on the TiO_2 surface was measured by the fluorescence spectroscopy. The obtained results showed that the photocatalytic activity in TiO_2 increased with increasing Ti^{3+} centers, but a significant increase in the yield of the photocatalytic reaction was observed for the sample prepared at 700°C, which had reduced rutile, even although it exposed a lower amount of Ti^{3+} than the sample prepared at 600°C. It was concluded that the presence of reduced rutile in TiO_2 enhanced much higher visible light activity than the reduced anatase.

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ABS44

From nano-to macro-auxetics: a simple three-parameter model of macroscopic auxetic structure inspired by penta-graphene

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Penta-graphene (PG) is a new carbon allotrope which has been proposed theoretically based on *ab initio* calculations [1]. The structure of PG resembles the well-known Cairo tiling, consisting solely of pentagons, which in PG are formed by carbon atoms connected with strong covalent bonds, both of the sp^2- and sp^3-type.

Since its discovery, PG has attracted much interest, mostly because of its unique electrical, optical and chemical properties. However, PG also possesses interesting mechanical properties, including but not limited to very high in-plane stiffness, comparable to that of graphene. PG is also predicted to be characterized by a negative Poisson's ratio [1–4]. Therefore, it belongs to a class of metamaterials called auxetics, which – due to their very unusual mechanical behavior and many possible practical applications – attract more and more attention nowadays.

Recent calculations [4] have shown that PG can be considered as a completely auxetic structure, as its Poisson's ratio (PR) is negative for all deformation directions lying in the plane of its structure. This feature is very rare, as most of the auxetic crystals display auxeticity only for some particular crystallographic directions. In [4] it has been also reported that the PR of PG decreases with the increasing strain, remaining negative even at very high strains. While both of the above-mentioned features make PG a particularly interesting metamaterial, its current practical applications are completely limited by the fact that it has not been synthesized yet. However, an attempt to transfer the mechanism of PG auxeticity into the macro-scale – and to build a macroscopic mechanical structure inspired by PG – can be made.

The presentation will aim to answer the question whether it is possible to produce a macroscopic equivalent of PG: a mechanical structure with a similar (*i.e.* pentagonal) topology and similar (*i.e.* auxetic) mechanical properties. For this purpose, a simple three-parameter model was proposed, within which the structure of PG was modeled as a network of nodes (corresponding to carbon atoms) connected with harmonic springs (corresponding to carbon-carbon bonds). The angular contributions (which capture energy changes originating from bending of bonds) were also included in the adopted model and also described using a harmonic potential. These contributions were found in [4] as essential for the auxeticity of PG.

Using the proposed model it was studied how its mechanical properties depended on its three parameters: two parameters defining the structure and one parameter describing the interactions. For this purpose, the elastic constants and the mechanical moduli were calculated using the molecular statics method. The relation between the parameters of the model and its mechanical properties was charactarized quantitatively and the region of auxeticity (for which $\mathrm{PR} < 0$) was determined. The results have shown that – despite its significant formal simplicity – the considered structure may display a complete range of mechanical behaviors, being even perfectly auxetic (with $\mathrm{PR} = -1$) or perfectly incompressible (with $\mathrm{PR} = 0.5$).

Although the proposed model is a considerable simplification of reality (the linear mechanical behavior of the model constituents is assumed) the obtained results strongly suggest that it should be possible to create a macroscopic equivalent of PG, which is also auxetic. The possibilities of manufacturing the proposed structure (*e.g.* using the 3D printing technology) will be also discussed during the presentation.

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ABS45

Magnetic nanomaterials for removal of heavy metals

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A new synthesis method for magnetic $Fe_3O_4/C/TiO_2$ nanomaterials was developed using microwave-assisted coprecipitation. The aim of the study was to examine the effect of an addition of various amounts of titanium dioxide on the adsorptive properties enabling removal of heavy metal ions from the solution. The materials were characterized with XRD, FTIR and BET. The adsorption of arsenic, lead and cadmium at the initial ion concentration of 10 mg/l was examined. The adsorption results are shown in Figure 1.

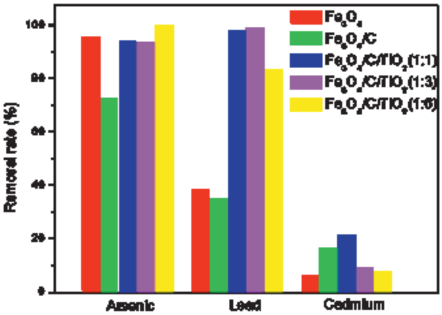

Figure 1. Arsenic, lead and cadmium removal degree

Materials modified with titanium dioxide showed better adsorptive properties than magnetite with carbon coating in the case of arsenic and lead. For cadmium, the best adsorptive properties were shown by the material modified with titanium dioxide at magnetite: the titanium dioxide molar ratio of 1 : 1.

Fully and partially bio-based aromatic-aliphatic copolyesters: structure and mechanical properties

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Without polymers, the present modern life would be impossible because polymers assure the high quality of life with the development of modern technologies. As a result the growing environmental awareness of the gradual exhaustion of non-renewable resources has stimulated the research for novel polymeric materials and production processes drawn from renewable feedstocks [1]. Hence, biobased monomers, obtained from plant biomass, are one of the main alternatives studied to obtain new kinds of polymers with similar or improved properties compared to the current fossil-based polymers [1]. Recent development of methods of synthesis of 2.5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF), which is obtained from carbohydrate biomass has resulted in increased interest in its use for syntheses of aromatic polyesters [2]. Sebacic acid is a natural C_{10} liquid fatty acid, directly produced from castor oil [3]. Bio 1,3-propanediol has been produced commercially since 2004, when DuPont with Tate & Lyle [4] developed a cheap technology of production of PDO from renewable resources (glucose obtained from corn starch). Homopolyesters such as poly(trimethylene sebacate) (PTS), and poly(trimethylene 2.5-furandicarboxylic acid) (PTF) are fully biobased, but poly(trimethylene terephthalate) (PTT) is at 37% by weight when made using annually renewable plant-based ingredients.

In this work, dimethyl esters of aromatic (FDCA) and aliphatic (SA) dicarboxylic diacids were used in synthesis of “green” copolyesters. Two series of random copolyesters were synthesized by a two-step polycondensation reaction in the presence of a highly effective catalyst at 230°C. The first series of poly(trimetylene 2.5-furanoate-co trimethylene sebacate) copolymers (PTF-*co*-PTS) containing from 5 to 25 wt% of trimethylene sebacate (TS) units and the second series of poly(trimetylene terephthalate-*co*-trimethylene sebacate) copolymers (PTT-*co*-PTS) containing from 15 to 50 wt% of TS units were obtained. The structure and composition of the obtained copolyesters were confirmed by ^{1}H-NMR spectroscopy. The phase structure of the obtained PTF-*co*-PTS and PTT-*co*-PTS copolymers was studied by differential scanning calorimetry DSC, dynamic thermo-mechanical analysis and X-ray diffraction spectroscopy. The study of mechanical and degradation properties of the obtained copolyesters showed that by changing the ratio of aromatic units (TF or TT) to aliphatic units (TS), random copolyesters which differ in mechanical properties and the ability to degradability

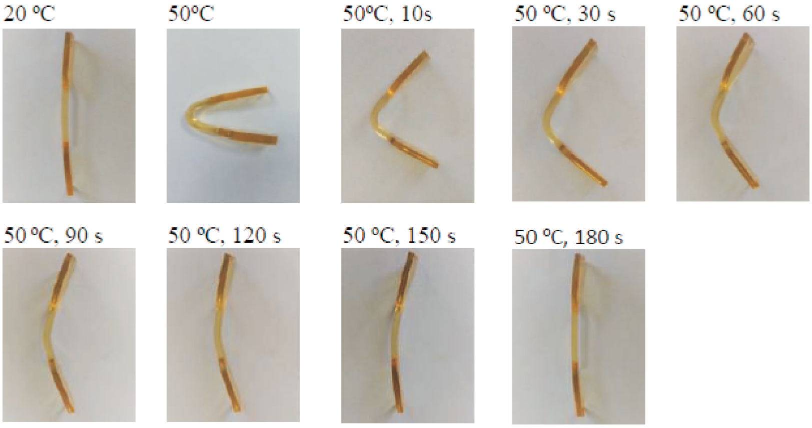

Figure 1. Demonstration of shape recovery of a sample (dumbbell) of PTF-*co*-PTS copolymer at temperatures above T_g

could be adjusted. It was found that one of the obtained PTF-*co*-PTS copolymers containing 15 mol % of PTS units with the glass transition temperature (T_g) of 28°C behaved as a shape memory polymer (SMP). Shape-memory polymers as stimuli-responsive shape-changing polymers are of great interest for fundamental research and technological innovation. It is known that shape memory materials display the ability of changing their shape in response to external stimuli. A PTF-*co*-PTS copolymer containing 15 mol % of PTS shows a thermoresponsive shape memory. For SMPs the time of reaching the original shape after recovery depends on temperature. It is known that SMPs at temperatures higher than T_g, enter the rubbery regime, characterized by a small Young's modulus and high deformability. In this region, the shape of an SMP can be modified and the modified shape can be preserved (or maintained) if the temperature is reduced below T_g [5]. If the SMP is once more reheated above T_g, the transition into the rubbery regime causes the SMP to regain its original shape.

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INDEX OF AUTHORS