Structural Studies of dielectric HDPE+ZrO₂ polymer nanocomposites: filler concentration dependences

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Abstract. Structural properties of HDPE+ZrO₂ polymer nanocomposites thin films of 80-100μm thicknesses were investigated using SANS, XRD, Laser Raman and FTIR spectroscopy. The mass fraction of the filler was 1, 3, 10, and 20%. Results of XRD analysis showed that ZrO₂ powder was crystallized both in monoclinic and in cubic phase under normal conditions. The percentages of monoclinic and cubic phase were found to be 99.8% and 0.2%, respectively. It was found that ZrO₂ nanoparticles did not affect the main crystal and chemical structure of HDPE, but the degree of crystallinity of the polymer decreases with increasing concentration of zirconium oxide. SANS experiments showed that at ambient conditions ZrO₂ nanoparticles mainly distributed like mono-particles in the polymer matrix at all concentrations of filler. The structure of HDPE+ZrO₂ does not changes up to 132°C at 1-3% of filler, excepting changing of the polymer structure at temperatures upper 82°C. At high concentrations of filler 10-20% the aggregation of ZrO₂ nanoparticles occurs, forming domains of 2.5μm. The results of Raman and FTIR spectroscopy did not show additional specific chemical bonds between the filler and the polymer matrix. New peaks formation was not observed. These results suggest that core-shell structure does not exist in the polymer nanocomposite system.
1. Introduction
In recent years a new generation of polymers such as high density polyethylene (HDPE) is being used as a matrix. The base polymers are reinforced with nanoparticle additives in order to improve the properties of polymer nanocomposites. In this case it becomes possible to adjust the structure and properties of the materials in wide range. The adding of inorganic spherical nanoparticles to polymer matrix allows the modification of the properties of polymers. These properties include physical, chemical, thermo mechanical, dielectric, optical and magnetic. Lastly, typical potential applications will be shown with the focus on new and innovative applications, like in energy storage systems [1].

ZrO\textsubscript{2} is one of the interesting oxide materials which is used as nanoparticle filler of the base polymers in order to improve their properties. This oxide material due to its hardness, optical transparency and high refractive index [2, 3] has already found a wide range of applications in different fields. These materials are used as interferometry filters in photonics, as a coating high power laser mirrors and atsetra. Pure ZrO\textsubscript{2} is a polymorphic material existing in three possible crystalline forms: monoclinic, tetragonal and cubic. The monoclinic phase is stable below 1170°C, the tetragonal at the temperature range of 1170-2370°C and the cubic at over 2370°C [4, 5, 6]. High strength and functionality make ZrO\textsubscript{2} filled nanoporous polymeric materials to develop highly relevant and attractive from an economic point of view. The unique stability of the ZrO\textsubscript{2} material to radiation opens up the prospects of creation on their basis of light high-strength and relatively inexpensive materials. This property can provide effective radiation protection of the navigation instruments of the spacecraft, instrument panels special equipment, working in conditions of high radiation background. The aim of this work is a comprehensive study of the structure of ZrO\textsubscript{2} filled nanoporous polymeric materials based on polyamides with the use of unique nuclear-physical methods. These studies will help to obtain new scientific knowledge and to approach the practical implementation of new structural and functional devices based on them [7, 8].

Polymer nanocomposites as a separate material, has a number of promising electrophysical [9], electret [10] and optical properties in applied approaching. These properties make them suitable for using for development for a new sensors, photovoltaic cells, piezomaterials, etc [11]. These types of nanocomposite materials have strong physical properties in comparison with ordinary polymers and leads to find wide application area. Polymer nanocomposites materials, based on a polymer matrix and inorganic ceramic nanoparticle fillers, have drawn considerable attention due to improvements in various properties. These properties include electrical, thermal, optical and other mechanical. The polymer nanocomposites materials are important to the electronic industry for its dielectric properties when used in capacitors. Polymer nanocomposites are considered constructual and industrial materials of the 21st century [12,13,14].

Addition of nanoparticles into polymer matrices remarkably changes thermal mechanical, optical, and electrical properties relative to the host polymer. Among these components are advanced capacitors that greatly require the advanced dielectric materials and film processing techniques. It has been well recognized that every new generation of capacitors have been primarily credited to the innovation and engineering of new dielectric materials [15]. The goal of this work was the investigation of the structure and interactions of HDPE+ZrO\textsubscript{2} in wide range of concentrations and temperatures.

2. Materials and methods
New high density polyethylene matrix samples (HDPE+ZrO\textsubscript{2}) were obtained using a crystal zirconium dioxide (ZrO\textsubscript{2}) particles of size 20-30 nm (Sky Spring Nanomaterials, Inc. Houston, USA [16]) with spherical morphology by thermal pressing method under pressure of 15 MPa and at a temperature of 165°C and then a sharp cooling in the water-ice system. Studied samples were made as thin film form. The spherical shaped ZrO\textsubscript{2} nano particles (20 ~ 30 nm) were used as a filler. The mass fraction of the nano filler was 1, 3, 10, and 20% in the polymer matrix. The thickness and the diameter of the samples were 80-100 μm and 5 cm, respectively. As a polymer matrix, it has been chosen powdered high-density polyethylene (powder-shaped stamps 20806-024) with an average molecular weight of 95·10\textsuperscript{3} g/mole, crystallinity degree of 65%, melting point of 130°C, and density of 958 kg/m\textsuperscript{3}. Selection of HDPE as a matrix is due to the fact that, it has a unique set of physical and mechanical properties, high wear
properties and impact strength, stability in harsh environments. The choice of HDPE is due to the low cost, adaptability, abundance and good dielectric properties [17, 18].

As a filler it has been used a crystal zirconium dioxide ZrO₂ spherical particles (Sky Spring Nanomaterials, Inc. Houston, USA) with size of 20~30 nm, specific surface area of S=35 m²/g and density of 5.68 g/cm³ [16]. Studied samples were made as thin film, the thickness and the diameter were 80-100μm and 5 cm, respectively.

Small-angle neutron scattering (SANS): Small-angle neutron scattering (SANS) measurements were performed at the time-of-flight YuMO spectrometer situated at IBR-2 pulsed reactor, JINR, Dubna, Russia [19, 20]. The experiments were carried out at sample-to-detector distances of 5.28 and 13.04 m, resulting in a Q range of 0.007–0.4 Á⁻¹ in the temperature range from 25°C to 132°C. The samples were kept in a special thermal box connected to a Lauda computer-controlled thermostat. The diameter of the sample in the beam was 14 mm. The measured neutron scattering spectra were corrected for the transmission and thickness of the sample, background scattering on the film substrate and on the vanadium reference sample using SAS software [21, 22, 23], yielding a neutron scattering intensity in absolute units of cm⁻¹. Measurements were carried out in the temperature range from 25°C to 132°C.

X-ray diffraction: The definition of phase composition and type of crystal structure has been performed on the conventional X-ray diffractometer EMPYREAN (firm PANalytical) in Cu- Kα radiation with Ni filter in the room temperature (25 oC). The operation mode of the device was 40 kV voltage and 30 mA current. The scanning has been done with a step of 0.026° and 2 s per step for 2θ. Analysis of phase composition and type of crystal structure of composite material has been performed using ICDD database.

RAMAN spectroscopy: Raman spectroscopic analyses can be applied for various materials, such as nanoparticles and polymer composites. This method is an important analytical and research tool which provides key information about polymer nanocomposites and material structure. Raman spectra were collected on a Horiba Lab RAM HR evolution spectrometer. Spectra were obtained in the wavelength range 3500-50 cm⁻¹. The instrument has two lasers: a HeNe laser with the emission lines at 633 nm and 325 nm from He-Cd. The HeNe laser was focused on the sample with a 100× objective in the experiment. Filter was not used during the measurements. HORIBA Scientific’s Lab Spec 6 software was used for complete instrument control and data processing.

FTIR Spectroscopy: To study structural changes in the samples, was used the technique of IR spectroscopy based on the measurement of transmission spectra of semi-transparent films. Spectra were obtained by the FTIR spectrometer of Shimadzu FT-IR in the wavelength range 4000-750 cm⁻¹. Samples for study were obtained in the form of thin films with a thickness of 80-100 microns size 8x30 mm² stage-by-stage pressing at a pressure of 6x10⁴ N/m² at room temperature using a special mold of Shimadzu.

3. Experimental

XRD study
X-ray diffraction (XRD) patterns of HDPE+20%ZrO₂, ZrO₂ powder and pure HDPE are shown in Figure 1. Observable diffraction lines of ZrO₂ coincide with monoclinic structure P 21/c1 of baddeleyite described early in reference [24, 33]. As shown in figure HDPE has two diffraction peaks when 2θ is between 20° and 25°. The 2θ with corresponding crystalline lattices for HDPE are 21.59°, 23.93°, 30.08° and 36.29° being composed of orthorhombic crystals and 2θ = 19.40° triclinic [32]. HDPE+ZrO₂ nanocomposites and ZrO₂ have identical crystalline lattices, except for 2θ = 21.59°. ZrO₂ does not affect the main crystal structure of HDPE. As a result, ZrO₂ and HDPE acquires monoclinic and orthorhombic phase, respectively.

From X-ray diffraction measurements it is determined that the structure of pure ZrO₂, as well as the structure of HDPE + 20% ZrO₂ nanocomposites has monoclinic symmetry and belonged to the space group of P1 21/c1 (14). The following values have been calculated for the crystal lattice parameters: a=5.149Å, b=5.210Å, c=5.318Å, α=γ=90°, β=99.215°, Z=4, V=140.832Å³. D spacing (lattice period) for the samples ranged between 1.4 – 5 Å. The results of XRD studies showed that the nano filler does not affect the crystal structure of the matrix when it is added to the polymer matrix at 1-3% of
concentrations, whereas at 10-20% structure of polymer became less crystalline, several diffraction peaks from polymer disappear.

![Figure 1](image_url)

**Figure 1.** X-ray diffraction (XRD) patterns of pure HDPE (violet), pure ZrO$_2$ powder (black), HDPE+3%ZrO$_2$ (blue) and HDPE +20% ZrO$_2$ (red) polymer nanocomposites

**SANS analysis**

The small-angle neutron scattering curves of HDPE+ZrO$_2$ (1, 3, 10 and 20%) and the pair distribution functions P(R) obtained from program GNOM (inset) are shown in Figure 2. It can be seen that P(r) does not change much as the ZrO$_2$ volume fraction increases. Total excluded volume $V_p$ (the aggregation volume), maximal length of nanocluster, number of aggregation ($N_{agg}$) were obtained using the data analysis software ATSAS 2.8.2 software program DAMMIF and Gnom [25, 26, 27]. The results are shown in Table 1. The average distance $D$ between ZrO$_2$ aggregates in the polymer matrix (1-20%) was obtained from eq.1, using the approximation of a primitive cubic lattice:

$$D^3 \varphi = V_p$$  \hspace{1cm} (1)

Where, $D$ is the mean distance between nanoclusters, $\varphi$ is the volume fraction of the filler and $V_p$ is the average volume of the nanocluster (see tab.1).
Figure 2. The small-angle neutron scattering curves of HDPE+ZrO₂, the pair distribution functions P(R) obtained from program GNOM (inset): a) 1,3,10 and 20% ZrO₂ at 25°C; b) 3%ZrO₂ at 25 - 132°C; c) 10%ZrO₂ at 25 -132°C

It is seen that the aggregation practically does not change with increasing of the ZrO₂ filler concentration and is about 1.5 of nanoparticles whereas for pure ZrO₂ powder the aggregation is about 4 nanoparticles. It means that for all concentrations of filler ZrO₂ nanoparticles are distributed in the polymer matrix homogeneously as monomers and separated by a high density polyethylene interlayer.
Table 1. SANS results obtained using the software DAMMIF and Gnom. Total excluded volume $V_p$, maximal length of nanocluster, the number of aggregation $N_{agg}$ ($N_{agg} = V_p / V_m$ here $V_p$ total excluded volume, $V_m$-volume of monomer) in the nanocluster. The volume fraction $\phi$ of ZrO$_2$, $D$ the average distance between nanoclusters for ZrO$_2$ in nanopowder / polymer matrix composites (1-20%).

| HDPE+ZrO$_2$ | Total excluded volume $V_p$, nm$^3$ | Maximal length of nanocluster, nm | Number of aggregation, $N_{agg}$ | Volume fraction, $\phi$ | $D$ the average distance between nanoclusters, nm |
|--------------|---------------------------------|---------------------------------|-----------------------------|----------------|---------------------------------|
| 1            | 0.876*10$^4$                    | 51.6                            | 1.2                         | 0.0018        | 169.5                           |
| 3            | 1.27*10$^4$                     | 61.6                            | 1.7                         | 0.0053        | 133.8                           |
| 10           | 1.12*10$^4$                     | 51.8                            | 1.5                         | 0.018         | 85.37                           |
| 20           | 1.07*10$^4$                     | 55.3                            | 1.5                         | 0.035         | 67.36                           |
| ZrO$_2$ powder | 2.82*10$^4$                    | 85.8                            | 4                           | ---           | ---                             |

As it is seen from Table 1. at 25°C ZrO$_2$ nanoparticles are distributed in the polymer matrix homogeneously as monomers and separated by a high density polyethelene interlayer for all concentrations of filler.

At small concentration of (1-3%) ZrO$_2$ the scattering behavior of polymer nanocomposite system does not changes with increasing of temperature up to 132°C (see Figure 2 b)), excepting the range of large Q scattering vectors—the region responsible for the scattering from the polymer matrix. The possible reason is that polymer became more amorphous at high temperatures. The changes of polymer structure in the composite system with temperature needs further detailed investigations.

At high concentrations 10-20% the scattering behaviour changes signficantly with temperature (see Figure 2. c)). The aggregation of ZrO$_2$ nanoparticles occurs with melting of polymer matrix.

At 25 °C scattering definitely shows Guinier region, whereas at the temperatures higher 82°C the scattering follows to Porod law:

$$ I(Q) = 2\pi \left( \rho_{ZrO_2} - \rho_{HDPE} \right)^2 \cdot Q^{-4} \cdot \frac{S}{V} = 2\pi \left( \rho_{ZrO_2} - \rho_{HDPE} \right)^2 \cdot Q^{-4} \cdot \frac{3}{R} $$

(2)

Where $\rho_{ZrO_2}$ and $\rho_{HDPE}$ are the scattering densities of ZrO$_2$ and polyethelene matrix. $S$ and $V$ are the surface and volume of the object with smooth surface, for spherical object $S/V$ ratio is $3/R$, where $R$ – is the radius of sphere. The spherical estimation of aggregation size from Porod law gives around 2.5μm.

Raman spectroscopy

Figure 3. shows Raman spectra for HDPE+(1-10%) ZrO$_2$, ZrO$_2$ powder and pure HDPE. The analysis of the Raman spectra showed that peak intensities depend on the filler contents.
Figure 3. Raman results for HDPE+(1-3-5-10%)ZrO$_2$, ZrO$_2$ powder and pure HDPE. a) 50 - 3500 cm$^{-1}$, b) 0 - 800 cm$^{-1}$ and c) 1000 – 1600 cm$^{-1}$interval was shown.

It should be noted that amorphous ν stretching C=C bonds are clearly seen for the with 1-3% filler content at 1081 cm$^{-1}$ point, but this is absent at 10% filler contents. The same process is also seen in crystalline+amorphous C-H$_2$ bonds at 1170 and 1370 cm$^{-1}$ for the with 10% filler content. However, the peaks in the range of 50 to 800 cm$^{-1}$ are assumed to be related to Zr-O- Zr bonds. These peaks are shown at 103, 180, 192, 335, 350, 383, and 476 cm$^{-1}$. As seen in Fig 3. b in the 50-800 cm$^{-1}$ spectral region at 25°C temperature the observed peaks as external mode 103, 180, 192, 223 cm$^{-1}$, internal mode 476, 504, 539, 560, 617, 639, 758 cm$^{-1}$ and intermediate spectral region 309, 335, 350 and 383 cm$^{-1}$ are the same as reported in this work [28]. The intensity of the peaks increases depending on the concentration of ZrO$_2$. This increase manifests for the 10% filler content. Vibrational phase and modes of the Raman spectrum of HDPE+(1-10%)ZrO$_2$ nanocomposites and pure high density polyethylene are summarized in the table 2. As shown in Fig 3. c in the 1000-1600 cm$^{-1}$ spectral region the Raman bands are assigned to the crystalline chain at 1063, 1130, 1295 and 1416 cm$^{-1}$ and the amorphous chain at 1081, 1440 and 1462 cm$^{-1}$ points. In the Fig 3. b in the 1000-1600 cm$^{-1}$ spectral region it is shown three distinctive peaks between 1400 -1500 cm$^{-1}$ (1416, 1440 and 1462 cm$^{-1}$). These peaks are assigned to the CH2 bending modes. The band at 1416 cm$^{-1}$ is also useful for estimation of the crystallinity of polyethylene. The 1440 cm$^{-1}$ and 1462 cm$^{-1}$ band are due to the CH2 bending modes of the amorphous trans chains and the melt-like amorphous chains, respectively. The Raman bands at 1295 cm$^{-1}$ and 1370 cm$^{-1}$ are assigned to the CH2 twisting modes of the crystalline and amorphous chains, respectively. These bands are used in the polymer matrix to estimate the crystallinity and molecular orientation. These results are very close to the results of authors [29-30] and confirm their results.
Table 2. Vibrational phase and modes of the Raman spectrum of pure HDPE and HDPE+(1-10%)ZrO$_2$ nanocomposites. Here is $\nu_{as}$ – asymmetric stretching, $\nu_s$ – symmetric stretching, $\tau$- twisting, $\delta$- bending, $\omega$- wagging chemical bonds.

| Raman shift, cm$^{-1}$ | Mode          | Phase                              |
|------------------------|---------------|------------------------------------|
| 1063                   | $\nu_{as}$(C-C) | Crystalline amorphous trans chain  |
| 1081                   | $\nu$(C-C)     | amorphous                          |
| 1130                   | $\nu_s$(C-C)   | Crystalline+amorphous trans chain  |
| 1170                   | $\rho$(CH$_2$) | Crystalline+amorphous              |
| 1295                   | $\tau$(CH$_2$) | Crystalline                        |
| 1370                   | $\omega$(CH$_2$)| Crystalline+ amorphous            |
| 1416                   | $\delta$(CH$_2$)| Crystalline(Orthorhombic)         |
| 1440                   | $\delta$(CH$_2$)| Amorphous trans (interphase)       |
| 1462                   | $\delta$(CH$_2$)| Amorphous(Intermediate)            |

FTIR Spectroscopy
Figure 4. Presents FTIR results for HDPE+ (1-3-5-10-20%) ZrO$_2$ and pure HDPE in the interval 4000 - 750 cm$^{-1}$ (see Figure 4. a). The bands chosen for HDPE+ZrO$_2$ polymer nanocomposites analysis were in the regions 700-750, 1400–1500, 2300-2400 and 2800–3000 cm$^{-1}$. In the 700-750 and 1420-1500 cm$^{-1}$ regions are shown doublet peak at 719.28, 731.07, 1462.07 and 1471.6 cm$^{-1}$ points (see Figure 4. b and c).

Figure 4. FTIR spectra of HDPE and HDPE+ (1-3-5-10-20%)ZrO$_2$ polymer nanocomposites
The absorbance peaks are located in a wide range of spectra scale. The first peak at 719.4, 729.5 cm\(^{-1}\) is C-H rocking deformation vibration, the second peak is for C-H bending deformation at 1461.6 and 1471.4 cm\(^{-1}\) doublet peak occurred due to the presences of some impurities on the sample. The next peak that is located at 1461 cm\(^{-1}\) respectively indicates aromatic C-H bond stretching vibration. The next peaks that are located in the region 2800-2950 cm\(^{-1}\) respectively indicate strong CH\(_2\) asymmetric and symmetric stretching vibration (see Figure 4.d). The peaks at 1306.1 cm\(^{-1}\) corresponds to twisting deformation, 1367.3 cm\(^{-1}\) to wagging deformation vibration \cite{31}.

The results of Raman and FTIR studies showed that there are no additional peaks in obtained HDPE+ZrO\(_2\) spectra compared with pure ZrO\(_2\) and HDPE samples. It indicates that there are no specific chemical bonds between the nano filler and the polymer matrix or the core-shell structure is not found in the polymer nanocomposite.

4. Conclusion

The results of XRD studies showed that the nano filler does not affect the crystal structure of the matrix when it is added to the polymer matrix at 1-3\% of concentrations. At 10-20\% of filler content, the structure of polymer becomes less crystalline as results of some of the diffraction peaks from polymer disappear. Any structural change does not occur. It is found that nanoparticles and HDPE have a monoclinic and orthorhombic structure in the polymer matrix. SANS experiments showed that at ambient conditions ZrO\(_2\) nanoparticles are mainly distributed as monomers in the polymer matrix and separated by a high-density polyethylene interlayer for all concentrations of filler. The number of aggregation is about 4 for the ZrO\(_2\) nano powder. The structure of ZrO\(_2\) nanoclusters does not change up to 132\(^\circ\)C at 1-3\% of filler content excepting changing of the polymer structure at temperatures upper 82\(^\circ\)C. At high concentrations of filler (10 - 20\%) the aggregation of ZrO\(_2\) nanoparticles occurs starting from 82\(^\circ\)C, forming ZrO\(_2\) domains of 2.5 \(\mu\)m.

The results of Raman and FTIR spectroscopy showed that there are no additional chemical bonds between the filler and the polymer matrix. New bands formation was not observed. The results showed that core-shell was not found in the polymer nanocomposite.

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References

[1] Thomas Hanemann, and Dorothée Vinga Szabó 2010 J.Materials 3 3468-3517
[2] M R N Soares, C Nico, D Oliveira, M Peres, L Rino, A J S Fernandes, T Monteiro, F M Costa 2012 Materials Science and Engineering B 177 712–716
[3] S Kumar, S Bhunia, A K Ojha 2015 Physica E 66, 74-80
[4] J C Garcia, L M R Scolfaro, A T Lino at. al 2006 J. Appl. Phys. 100 104103-104109
[5] Chevalier J, Gremillard L, Virkar A V at. al 2009 J. Am. Ceram Soc 92 1901-1920
[6] Suresh A, Mayo M J, Porter W D at. al 2003 J. Am. Ceram. 86 360-362
[7] Geethalakshmi K, Prabhakaran T and Hemalatha J 2012 International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering 6 4 256-259
[8] Shruti Nambari and John T W Yeow 2012 ACS Appl. Mater. Interfaces 4 11 5717–5726
[9] Tyutnev A P, Saenko V S, Pozhidaev E D at. al 2005 Dielectric properties of polymers in the fields of ionizing radiation Under ed. N S Kostyukova Book 5 M Nauka 453
[10] Gorokhovatskiy Y A, Aniskina L B, Burda VV et. al 2009 Proceedings of Russia pedag.university named after A.I.Gertsen, Scientific journal 95 63-66
[11] Guo N, Sara A Di Benedetto at. al 2010 J.Chem. Mater. 22 4 1567-1578
[12] Najiba Abdullah Al-Hamadani, Noor Dhaief Al-Shwak 2015 IOSR Journal of Applied Physics
72278-4861

[13] Selyutin G E, Gavrilov Y Y, Voskresenskaya E N et al 2010 Chemistry for sustainable development 18 375-388
[14] T Tanaka 2005 IEEE Transactions on Dielectrics and Electrical Insulation 12 5 914-928
[15] Daniel Tan, Yang Cao, Enis Tuncer, Patricia Irwin 2013 Materials Sciences and Applications 4 6-15
[16] www.ssnano.com
[17] M M Guliyev, R S Ismayilova, A A Nabiye 2016 Journal of Radiation Research 3 №1 14-23
[18] Guliyev M M, Maharramov A M, Ismayilova R S, Nabiye A A 2015 Perspective materials 7 17-22
[19] Yu M Ostanevich 1988 Makromol.Chem.Macromol.Symp. 15 91-103
[20] A I Kuklin, A Kh Islamov and V I Gordeliy 2005 Neutron News 16 16
[21] A G Soloviev, T M Solovieva, A V Stadnik, A Kh Islamov, A I Kuklin 2003 Communication of JINR P10-2003-86
[22] Kuklin A I, Rogachev A V, Soloviov D V, Ivankov O I, Gordeliy V I 2017 IOP Conf. Series: Journal of Physics 848 012010
[23] Soloviev A G, Solovjeva T M, Ivankov O I, Soloviov D V, Rogachev A V, & Kuklin A I 2017 IOP Conf. Series: Journal of Physics 848 012020
[24] Arashi H, Takeda H, Kudoh Y 1986 Powder Diffraction 1 265 - 275
[25] Svergun D I 1992 J. Appl. Cryst. 25 495-503
[26] D Franke and D I Svergun 2009 J.Appl.Cryst. 42 342-346
[27] D Franke et al. 2017 J.Appl.Cryst. 50 1212–1225
[28] You Ling-Lin, Jiang Guo-Chang, Yang Song-Hua, Ma Jin-Chang, Xu Kuang-Di 2001 Chin.Phys.Lett. 18 7 991-993
[29] Takumitsu Kida, Yusuke Hiejima and Koh-hei Nitta 2015 IntJ.Exp. Spectroscopic. Tech 3-6
[30] Saverio Affatato, Enrico Modena, Simone Carmignato, Paola Taddei 2013 ELSEVIER Wear 297 781-790
[31] J.V. Gulmine et al. 2002 Polymer Testing 21 557–563
[32] E R Walter and F P Reding 1956 J.Polymer.Sci. 21 561
[33] Gauna M R, Conconi M S, Gomez S, Suárez G, Aglietti E F, Rendtorff N M 2015 Journal Ceramics – Silikáty 59 4 318-325