



DEVELOPMENT OF TECHNOLOGY FOR CREATING POLYMERIC COMPOSITE MATERIALS BASED ON POLYVINYLIDENFTORIDE AND DISPERSED FILLERS

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Introduction

The development of modern technology – mechanical engineering, electronics, electrical engineering, radio engineering and other industries-requires the development of a new type of polymer composite materials with such functional characteristics as electrical conductivity, dielectric and magnetic conductivity, etc. Time has high strength, flexibility, low weight and thickness, which is especially characteristic of materials that protect against electromagnetic radiation, is known to us. Currently, Composite fibers are increasingly used to solve the problem

ABSTRACT

In this study, the introduction of various forms and types of functional fillers and directed structure formation in the process of production and appropriate processing of primary fibers, and the creation and implementation of cheap and multifunctional form of composite materials. It is based on the analysis of scientific research on the synthesis and structure of composite materials, as well as the introduction of various fillers into the selected polymer. Polyvinylidenftoride is a fluorine polymer with excellent mechanical and electrical properties, which, due to its application in a wide range of industries, was chosen as the main material in the study . Also aimed at the development of polymer compositions based on Polyvinylidenftoride and disperse fillers. The synthesis of these composites was obtained by distributing ceramic powders in N-methyl-pyrrolidone (solution by mechanical mixing and ultrasound until a homogeneous mixture is obtained.

of creating such materials, combining the special properties of various dispersed fillings and the high physical and mechanical properties of a directed fiber-forming polymer.[1]

The composite materials used in the creation of radio engineering structures have certain electrodynamic properties, in particular, they require different types of fibers with an electrical conductivity level of up to $10^{-r-101} (\bar{O} \text{ cm})^1$. To obtain fibers with the necessary electrodynamic properties, it is necessary to enter the maximum possible number of functional fillings of various types into the fiber-



forming polymer. The physical and mechanical properties of such fibers should be sufficient for their use. From the analysis of many experimental and theoretical works, it can be seen that the electrical properties of composites, such as electrical conductivity, dielectric and magnetic conductivity, are most susceptible to changes in the winding of particles in the composition, especially in cases where the included fillers have both, this is clearly noticeable. [2]

Practical significance of the work. Development of approaches for creating composite materials based on Polyvinylidene fluoride and dispersed fillers with variable electrophysical properties by introducing functional fillers of various shapes and types and directed structure formation during the production and corresponding processing of primary fibers.

Analysis of literature on the topic

Currently, polymer matrices used to obtain composite materials must meet a number of requirements. When choosing a matrix, the following should be taken into account: characteristics of the Matrix, compatibility with the selected filling phase, characteristics given to composites, the possibility of using and durability of the Matrix and composite [3].

Disperse fillers are the most common type of PCM fillers, they are various substances of an organic and inorganic nature. One of the main goals of dispersed fillings is to reduce the cost of compositions. Basically, these are powdery substances with different particle sizes – from 2-10 to 200-300 microns. Typically, the particle size does not exceed 40 μm , but particles smaller than 1 μm have recently been used to create nanocomposites. The content of

dispersed fillings in PCM varies in a wide range – from a few percent to 70-80%. Such PCMs, as a rule, are isotropic; however, the asymmetric shape of the particles, if they are significantly oriented during processing, can lead to the appearance of anisotropy of some properties – the latter is characteristic of fibrous fillers.

Among the polymers that have been used for many years, Polyvinylidene fluoride (PVDF) is of particular interest, most often it is used as a matrix with filler materials and has the best known piezoelectric properties among polymer materials. [4]

Polyvinylidene fluoride (PVDF) is an amorphous semi-crystal with a complex structure. In addition, PVDF forms different crystalline phases (a, b, g, and d) or II, I, III and IV, which are related to different molecular configurations and have different forms in lattice type and chain conformation.

Among inorganic materials, piezoelectric ceramics are often used as a filler due to its special properties (high piezoelectric coefficients, low dielectric and mechanical losses, good thermal properties, a large range of dielectric conductivity) due to the advantages (low) of polymers. Density, high resistance, excellent mechanical properties, shaping and low cost) improve the final properties of the resulting composition.

In general, piezoelectric ceramics include barium titanate, bismuth titanate, lead magnesium niobate, lead methaniobate, lead nickel niobate, lead zinc titanates (PZT), lead-lanthanum zirconate titanate (PLZT), and niobium lead zirconate titanate (PNZT). Synthesis pathways play a crucial role in the properties of piezoelectric ceramics. A literature study has shown that



there are many physical methods (metal-organic chemical vapor deposition or pulsed laser deposition) that are successful in growing high-quality ultra-thin oxide films, but these methods are ineffective for deposition. Large substrate surface chemical methods have attracted attention lately, they are more suitable for simpler control of composition and sediment film uniformity, as well as optimization of processing conditions. One of the important advantages was the ability to obtain powders with fine microstructures, but are also available at lower synthesis temperatures. Therefore, piezoelectric types of ceramics, thin films and their ferroelectric, piezoelectric and dielectric properties are criteria that highlight the prospects for various processes that can affect the behavior of selected special devices. [5]

In the literature devoted to this topic, there is information about the distribution of various piezoelectric ceramics in polymeric matrices, which can be used in a wide range. PZT-PVDF composites were prepared by initial dispersion of PZT powder into various solvents (ethylmethyl ketone - MEK, N, Ndimethylformamide, toluene-ethanol, MEK-ethanol (azeotropic), xylene-ethanol, etc.), or by surface of pyesoceramic particles using 3-metacryloccipropyl-trimetoxy silane (KH-570) and isopropyl dialeic (diocylphosphate) titanium (NDZ-101) was created by changing with a type of binding agent, then mixing with a matrix and mixing with PVC.[6]

Methodology

In the preparation of the article, many electronic and written sources were studied on the topic, and traditional and

modern methods were studied on the creation of composite materials.

The most important methods for obtaining composites based on polyvinylidenftoride and dispersed filler components are achieved through in situ and ex situ synthesis. In situ synthesis allows the production of composites by decomposing corresponding metal precursors, which is an effective way to prevent particle agglomeration by ensuring good spatial distribution of particles in the polymer matrix. The second approach is eks situ synthesis, which is synthesized until nanoparticles are introduced into the polymer as a dispersion medium. The most commonly used methods of dispersing nanoparticles in a polymer matrix are direct mixing of powders with a matrix, in situ polymerization in the presence of synthesized particles, in situ deposition of inorganic components or polymer structure, composites formed by adding nanoparticles to the PVDF Matrix enhance performance and synergistic applications, which cannot be provided separately by polymer matrix or nanoparticles [6]. Among inorganic materials, piezoelectric ceramics are often used as a filler due to its special properties (high piezoelectric coefficients, low dielectric and mechanical losses, good thermal properties, a large range of dielectric conductivity) due to the advantages (low) of polymers. Density, high resistance, excellent mechanical properties, shaping and low cost) improve the final properties of the resulting composition. [7]

Research progress

In this work, we will consider the synthesis of PVDF-PZT composites based on a composition suitable for the production of micro-biosensory membranes as a



dispersive filler obtained by traditional methods, as PZT particles and a polymer matrix in the N-methyl-pyrrolidone (NMP) of PVDF. Features of piezoceramic fillings before and after polymer matrix absorption were examined by the Fourier transform Infrared Spectrometer, field emission scanning electron microscope and X-rays were seen in diffraction.

In our experiments, we used PZT powder as a filler obtained in the traditional way (hydrothermal synthesis). Polyvinylidene fluoride or PVDF - $(C_2H_2F_2)_n$ - (average M.li granules ~ 180.000) was chosen as a polymer matrix for composites (from Sigma-Aldrich, all analytical level). N-methyl-2-pyrrolidone (NMP) (C_5H_9O , M w = 99.13 g/mol) was used as a solvent to dissolve PVDF and distribute PZT.

Experiments designed to obtain composites were carried out in three stages. The first step was to dose and distribute PZT ceramic particles in the Matrix afferent solvent to prevent particle agglomeration and increase their compatibility with The Matrix. PVDF solution was obtained by dissolving in NMP to obtain an optimal concentration of 5% (w/v). For this purpose, melting was carried out by heating and magnetic mixing, the temperature is maintained at $70^\circ C$ until the fluoropolymer is completely dissolved.[8]

Finally, after dissolving the PZT particles and dissolving the PVDF matrix, the two components were brought into contact by adding ceramic dispersion to The Matrix and then continuous mixing at $60^\circ C$ and ultrasonication at room temperature.

In the process of optimizing the dispersion of PZT particles in a polymer matrix, it is determined that the optimal ratio is 1:10. So the resulting composition is laid out in

the form of a film with a thickness of 5 cm. At a thickness of $7 \mu m$, it is kept in the oven at $100^\circ C$ for 4 hours to completely remove the solvent. This composite material is considered ideal for obtaining membranes for the development of microbiocensors.[9]

The binding configuration of PZT powder, PZT (NMP) in the solvent, PVDF Matrix (NMP) in the solvent, and PZT-PVDF-NMP was studied using the Fourier Transform Infrared Spectrometer (FTIR) in the number of waves using the Bruker Tensor 27 spectrometer. In the range of $4000-400 CM^{-1}$ with 64 scans up to 4cm. Phase identification of samples (PZT powder, PZT-NMP, PVDF-NMP and PZT-PVDF-NMP) the rotating anode SmartLab diffraction system is equipped with a CuK α 1 tube and a multi-layer mirror ($\lambda = 1.541867 \text{ \AA}$), 2 t in heating from 5° to 90° . [10]

The morphology and micro-structure of PZT filler, PVDF polymer matrix and PZT-PVDF composites were carried out using Del emission scanning electron microscopy (FE-SEM). The Sam image was obtained using the FEI Nova NanoSEM 630, equipped with a TLD detector and HV up to 15-20 kV. Sam evaporated on the gold layer sample surfaces to improve image quality.[11]

Results and discussion

Structural analysis

With the help of measured vibration frequencies, chemical bonds from the composite material, matrix and PZT-PVDF composition were studied. The normal atmospheric FTIR spectra of the PZT filler, polymer matrix - PVDF and PZT-PVDF Composite are shown in Figure 1. The PHTIR spectrum of the PZT filler indicates peaks up to about $500 cm^{-1}$, which can be assigned to the Ti-O-Ti stretching vibration

mode from a piezoceramic structure. In the case of dispersion of PZT powder in the corresponding solvent, we can also observe the appearance of the characteristic absorption band (NMP) of the solvent, which is observed at 2945 CM i.e. - 1(symmetric stretch) and 2882 cm-1(asymmetric stretch) vibration property of the CH Group; 1686 CM-1specified C = O (asymmetric elongated vibration) and 1305 CM-1N contact with.[12]

The FTIR Spectra recorded for PVDF and PZT-PVDF composite samples are described in Figure 1. Absorption ranges in the PVDF Matrix 1297, 1175, 982, 850, 750,

619, 533, 43 can be defined in CM.- Characteristic of Phase 1a. The suction line from 750 CM-can be associated with oscillating oscillations in the 1pvdf chain. 619 cm-1, it can be assigned to the bending oscillation of CF2, and the bending and flutter oscillations of 433 CM-1cf2 groups belonging to the A-PVDF Polymorph are manifested [13].

The PHTIR spectra for PZT - vdf composition confirm the existence of a -.the phase corresponds to the addition of total PZT powder to the polymer matrix as the dominant phase without any change in the spectrum.

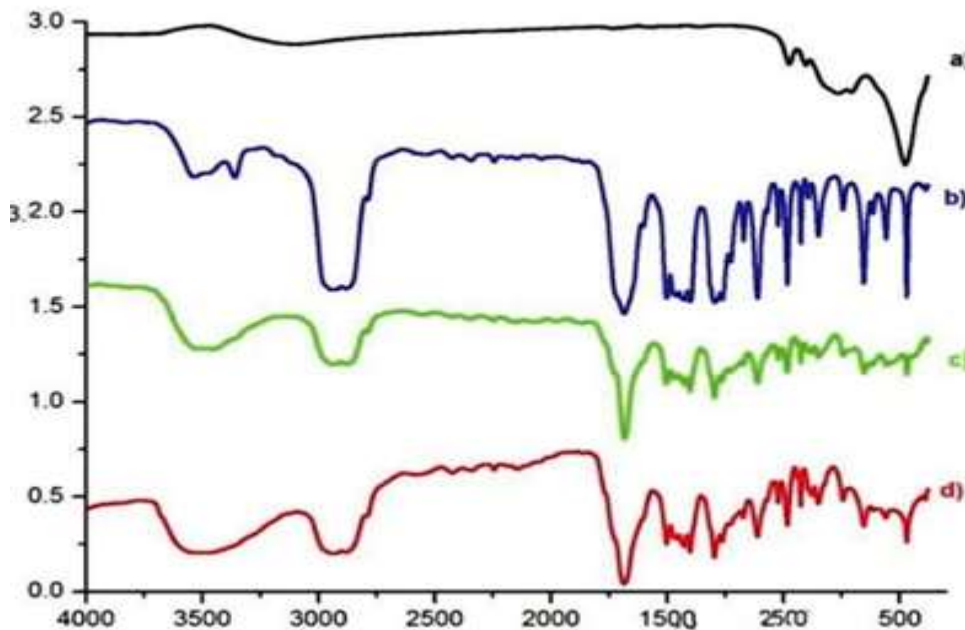


Figure 1. FTIR spectra of PZT powder (a) PZT-NMP (b), PVDF-NMP (c) and PZT-PVDF-NMP composites (d)

To confirm the crystal phase of the samples and the effect of PZT ceramic particles on the polymer matrix, an X-ray diffraction analysis of 5 ° to 90 ° was carried out, as shown in Figure 2.

The PZT powder sample shows the observed characteristic peaks 2 T =9,7 °, 11,7 °, 14,1 °, 24,2 °, 30 °, 32 °, Miller indices (001), (200), (201), (110) corresponding to the planes in which 33,3

°, 44,2 °, 48,2 °, 52,4 °, 56,4 °,(112), (311), (203), (313), (020), (022), (421).

The powder sample is indexed and purified in a monoclinic cell in the C12/m1 Space Group, and the lattice parameters are a=15.1830 A, b= 3.7830 A, c=9.1430 A. The size of the crystallite was calculated at the strongest peaks (2T =11.7 °) using the Scherrer formula and it was determined that it was 24 nm. Other researchers [7], [13], according to research carried out for The Matrix sample (Figure 2C), five peaks that clearly confirm apdv phase are highlighted.

The most prominent peaks are respectively $17,5^\circ$, $19,8^\circ$, $26,6^\circ$, $36,2^\circ$ and they are at $38,6^\circ$ (020), (110), (021), (200) and (210) can be included in the plains. On-at the stage of the PDV, characteristic peaks of the plains are observed. It appears as shoulders at about 17.5° and 19.8° . The XRD pattern of the PZT-PVDF composite sample is shown in Figure 2D. It is noted that in addition to the characteristic diffraction peaks of the PVDF matrix from 17.5° to

26.6° , the PZT filler is also used in the 2th = $9,7^\circ$, $11,7^\circ$, $\sim 30^\circ$ and there are characteristics at $\sim 48^\circ$, indicating that two phases coexist in synthesized compositions.[14]

When comparing PZT powder with PZT-PVDF composites, it was found that there is no additional evidence of structural changes confirming the addition of particles to the polymer matrix. XRD analysis is well suited to FTIR analysis.

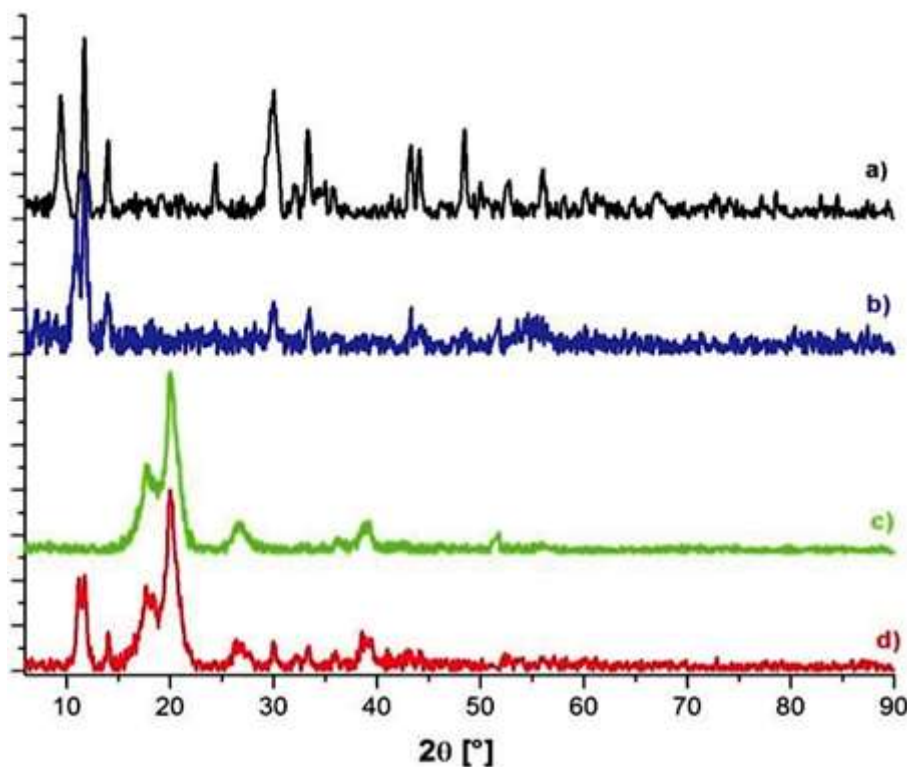


Figure 2. XRD sample of PZT powder (a) PZT-NMP (b), PVDF-NMP (c) and PZT-PVDF-NMP composites (d).

Morphological analysis

The morphology, size and dispersion of PZT particles in the solvent (NMP) and PVDF polymer matrix was carried out by FE-SEM (field emission scanning electron microscope), respectively. Images of samples (PZT, PVDF and PZT-PVDF composition in the solvent) are presented in Figure 3 (ad) and analyzed separately to understand the effect of the filler on

morphological characteristics, distribution in the selected polymer matrix.

SEM images of the PZT filler (Figure 3A) suggest that this type of material appears as fibers with dimensions in the order of several tens of microns in length, and their width varies between 15-60 nm. Also, by distributing the filler substance in the appropriate solvent (NMP) (Figure 3B), the morphology of the filler was preserved in the form of fibers, the diameter of which was not affected by the type of solvent or the processing conditions. In addition, the

average volume of fibers after dispersion was compatible with the filler and keeps their volume in the same range.[15]

The polymeric matrix of PVDF in the Afferent solvent (Figure 3C) shows an inhomogeneous structure with the presence of relatively large gaps / gaps on the surface of the deposited layer. In the case of the addition of the PZT filler to the PVDF Matrix (Figure 3d), the morphology

was not affected (scattered and smooth nanotoles were obtained), as well as the length of the fibers remaining in the same range. The SEM image of PZT-PVDF composites determined that the PZT filler is better distributed within the PVDF matrix, the fibers have a symmetrical orientation compared to the filler materials.[16]

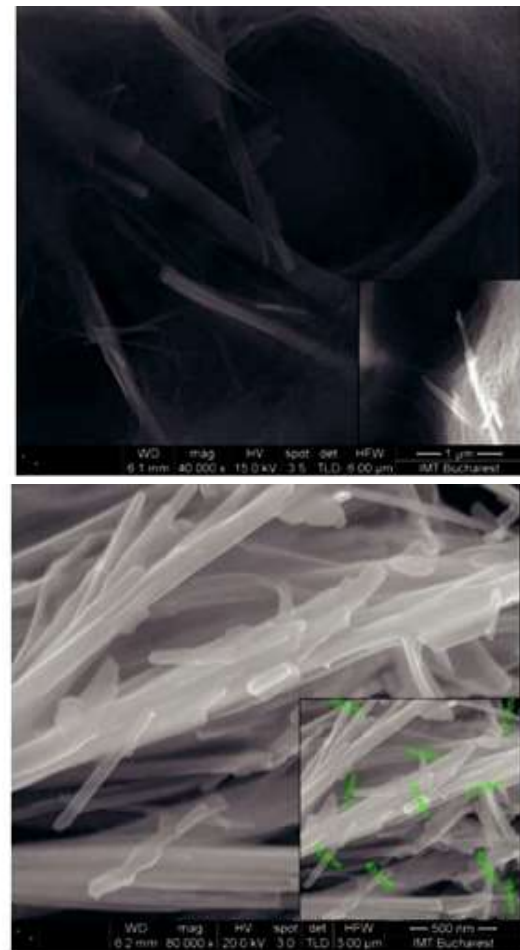
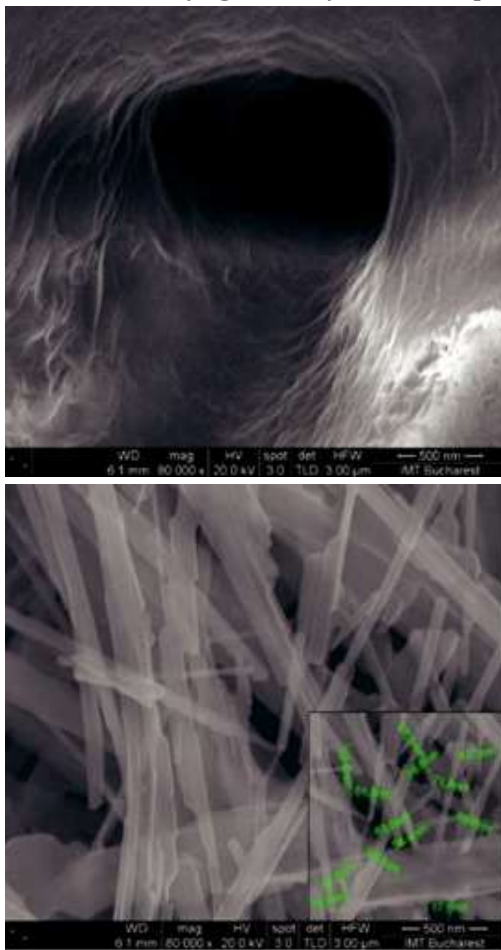


Figure 3. SEM micrography of PZT powder (a) PZT-NMP (b), PVDF-NMP (c) and PZT-PVDF-NMP composites (d)

Conclusions

The PZT ceramic powder and PVDF polymer matrix obtained by the traditional method for obtaining PZT-PVDF composites were dispersed in the NMP solvent. After that, PZT-PVDF composites were prepared by ex situ synthesis.

The properties of the piezoceramic filler before and after dispersion in the solvent were studied before the introduction of PVDF into the polymer matrix. The FTIR spectrum showed the total input of the PZT filler into the matrix while maintaining the absorption band properties for Phase a of PVDF. XRD confirmed FTIR spectra that the polymer matrix has the same phase of PVDF. In addition, the composite XRD spectrum showed that there were no



structural changes, so the addition of particles to the polymer matrix was confirmed. In SEM images, it was observed that the PZT complement retained its morphology and size in the same nanometric range even after being inserted into the PVDF Matrix. PZT-PVDF composites open up new opportunities for the development of large-scale production of membranes for micro-biosensors with technological applications.

On the basis of magnetic and electrically conductive Polyvinylidenefluoride and dispersed fillers, approaches have been

developed to obtain copositional materials, and their structure, physico-mechanical and electrophysical properties have been studied in wide concentrations.

A characteristic feature of the structure of the composite material after molding was determined by the high porosity and orientation of the anisometric filling. These factors determining the degree of electrophysical properties of a magnetic-filled VPK are regulated by the conditions of molding and subsequent processing.

References:

1. H. Who and others, *J. Compos. Mater.* (2017) doi.org/10.1177/0021998317704709.
2. S. Li, M. Meng Lin, MS Toprak, DK Kim, M. Mohammed, *Nana Rev.*1., 1 (2010).
3. X. Zhao, L. Lv, B. Pan, V. Zhang, S. Zhang, Q. Zhang, *Chem. Most. J.*1, 2–3 (2011).
4. R. Li, X. Wang, P. Wang, X. Liu, J. Pei, *Mater. Ekspress*6, 526-534 (2016).
5. V. Tochoreanu, A. Matei, AM Avram, I. Mihalache, M. Papesko, B. Bitu, B. Tingo, M. Danila., *EMRS* (2016).
6. S. Maharana, MG Mishra, B. Behera, RN Mahaling, J. Vixar, J. Vihar, *Int.J.Application.Innov.Most.Manage.*3, 303-315 (2015).
7. IA Al Ajaj, FT Naori, NN Ramao, *J. Macromolec. Sci.*2, 79-88 (2013).
8. V. Ma, J. Zhang, S. Chen, X. Wang, *J.Macromole. Sci. Part B*47, 434-449 (2008).
9. Jain, KJ Prashanth, JK S, AK Sharma, *Int. J. Mater. Sci. Most.*3, 327-345 (2016).
10. Tsonos and others.*Express Palim. Lett.*9, 12, (2015).
11. X. Sir, X. Wang, Y. Zhou, L. Zhang, *Prog. Nat. Sci. Mater. Int.*22, 250-257 (2012).
12. MA Hud, M. Marie, R. Muñoz-Espi, *Materials* 7, 4057-4087 (2014).
13. Q. Guo and others.*Polymers*6, 2037-2050 (2014).
14. K. Kaushik, NK Sharma, *J. Med. Sci.*2, 52-58 (2014).
15. V. Tochoreanu, A. Matei, I. Mihalache, M. Danila, M. Papesko, B. Bitu, *J. Mater. Sci.*50, 1883-1890 (2015).
16. Ingrosso, AM Panniello, R. Comparelli, ML Curri, M. Striccoli, *Materials* 3 (2010).