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PVDF FILM WITH HA, PHA, AGNO$_3$ FILLERS FOR BIOCOMPATIBLE PIEZOELECTRIC SENSORS

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Abstract: *Biosensors are usually prepared from ceramics and polymer composites. Materials polyvinylidene fluoride - PVDF, hydroxyapatite - HA, polyhydroxyalkanoates - PHA and silver nitrate – $AgNo_3$, have properties very suitable for biosensors. Due to its well-known superior ferroelectric characteristics and biocompatibility, PVDF polymer has been widely used in several applications. Its applicability is restricted by hydroxyapatite's brittleness and weak bending strength. Numerous formulations for HA and polymer composites have been devised to make up for the mechanical weakness of HA. Because there is so much HA in the final product, HA/polymer composites are very biocompatible. The maximum piezoelectric activity is produced when an appropriate amount of silver is deposited, and silver nitrate has antimicrobial qualities. PHA's are biocompatible, biodegradable, and exhibit piezoelectric and nonlinear optical properties, which can be useful for tissue engineering, drug delivery, biodegradable packaging, and smart materials. These materials were chosen to create functional element – film. The non-toxic solvent DMSO (dimethyl sulfoxide) and the solvent casting method for preparing the thin film were chosen for the preparation of the film. Hydrophilicity and surface roughness were chosen to measure the properties of the thin film.*

Keywords: PVDF, Solvent casting, Film, Hydrophilic, Surface roughness.

1. Introduction

Materials with piezoelectric properties are beneficial for various applications. They can be used in automotive technology, medical industries technology (Koller, 2020). The usage of polymer materials or composites has become increasingly necessary. Because they are readily available and more cost-effective than other materials, polymer composites enable versatility in terms of product qualities, starting raw material alternatives, design, and gradually developing advancements in fusion processes (Al Rashid et al., 2021).

Polyvinylidene fluoride (PVDF) polymer has been widely hired in some applications because of its recognized good ferroelectric properties (Ribeiro et al., 2012). The primary mineral in bones is hydroxyapatite (HA), a calcium phosphate crystallization that occurs naturally. Natural hydroxyapatite and bone have physical, chemical, and biological properties that make them compatible (Shanta, 2018). The polyhydroxyalkanoates (PHA) is it close to plastics hence PHA bioplastic makes a good alternate which is biodegradable and biocompatible (Rutika, 2020). PHAs are biocompatible, biodegradable and demonstrate piezoelectric and non-linear optical properties making them potential useful for tissue engineering, drug delivery, degradable packaging and smart materials.

PVDF polymer and α-PVDF/HA composites mechanical properties and biocompatibility can be used for medical and dental applications or other industries (Ribeiro et al., 2012). Aim of this research is create antibacterial functional element and uses these potential materials.

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2. Material and methods

Since PHA - polyhydroxyalkanoates is so similar to plastics, it is a good replacement that is also biodegradable and biocompatible. PHAs are chemically in vivo polymerized hydroxyalkanoates, which are made by microorganisms. PHA is the main mechanism for bacteria' survival and aids in their ability to endure environmental stress. When bacteria are exposed to freezing and thawing, osmotic shocks, oxidative pressure, desiccation, H_2O_2 – hydrogen peroxide supply, heavy metals, and UV (ultraviolet) rays, PHA may provide defensive mechanisms (Rutika, 2020).

PHAs have the potential to be beneficial for tissue engineering, medication delivery, biodegradable packaging, and smart materials due to their biocompatibility, biodegradability, and piezoelectric and non-linear optical capabilities. PHAs have certain intriguing physical characteristics, including piezoelectricity, non-linear photonic activity, biocompatibility, and biodegradability (Fabricio et al., 2018, Koller, 2020).

Silver - Ag is one of the inorganic antibacterial agents that have been extensively studied recently. Silver is believed to be antibacterial through formation of silver ions - Ag+. To obtain the antibacterial effect of silver ions, heavy metals react with proteins by binding to thiol groups, resulting in protein inactivation.

Ag+ released from silver nanoparticles - Ag0, interact with phosphorous moieties in DNA-deoxyribonucleic acid. In fact, Ag0 are highly germicidal, quite harmless to humans, and nontoxic. Even the highest concentration of nanosilver causes no side effects.

The addition of a conductive phase such as Ag can be beneficial because; first, the conductive phase improves the charge transfer by increasing the sensitivity of the piezoelectric response and a suitable amount of Ag deposition gives the piezoelectric activity, while a higher Ag loading decreases the piezoelectric activity (concentration properties studied 0.12, 0.21, 0.52%, 1 ml) (Soroush et al., 2021).

Piezoceramic materials are the basis of key engineering components in the fields of biomedical devices, acoustics, microelectronics and sensors. The engineering requirements for piezoceramics with complex geometries have increased significantly, requiring higher efficiency (Smirnov et al., 2021).

Hydroxyapatites - HA is a naturally occurring mineral form of calcium apatite comprising of about fifty - 50% of the volume of the bone. One of the most common apatite's used as bio ceramic in medicine industry and dentistry industry is HA due to its bioactivity and osteoconductive properties. Chemical formula of hydroxyapatite - $Ca_5(PO_4)_3OH$ but usually written as $Ca_{10}(PO_4)_6(OH)_2$. Natural HA can be prepared from eggshells, fish bone, coral, chicken bone, etc. (Ribeiro et al., 2012).

Synthetic HA exhibited high porosity, low crystallinity. On the other hand, HA obtained from animal bone via calcination at 800˚C possesses highest crystallinity. HA has the capacity to form chemical bonds with ambient hard materials with the forming of a HA interfacial ply. The similar chemical and physical characteristics of natural HA with bone do it biocompatible (Ribeiro et al., 2012).

DMSO - dimethyl sulfoxide is an aprotic solvent that also miscible with polar solvents because it has a dipole moment. It can dissolve lipophilic molecules such as PHA and can easily penetrate biological membranes. These properties make DMSO a potential solvent for the extraction of PHA from bacteria and the solubilization of other polymers.

PVDF - polyvinylidene fluoride films with high content of β-phase up to 98.8% are obtained by using DMSO as the solvent at optimized crystallizing temperature of 60 °C. The corresponding PVDF film with high β-phase content presents excellent ferroelectric and piezoelectric properties. Finally, PVDF films can be prepared by solvent casting. To evaluate the effect of crystallization temperature on the amount of β-phase, different crystallization temperatures (50–160 °C) can be applied to prepare PVDF films using the optimal DMSO solvent (Xiongjie et al., 2019). The same polar solvent can form all three phases of PVDF. Different phases of PVDF can be obtained by changing the solution temperature using the polar DMSO solvent. Annealing conditions lead to the presence of different phases and the transformation of one phase into another PVDF phase. The β-phase, which is important for ferroelectric applications, is obtained by using a polar solvent and appropriate annealing. The maximum β phase in the films exists when the PVDF films are annealed at 90°C for 5 h. (Satapathy et al., 2011).

2.1. Preparing process

Films are obtained using DMSO - dimethyl sulfoxide as a solvent at an optimized temperature of 80 °C. PVDF - polyvinylidene fluoride and PHA - polyhydroxyalkanoates beads and DMSO solvent were first mixed and dissolved at 80 °C for 4–5 h until a homogeneous solution was formed. Silver nitrate – $AgNo_3$ and hydroxyapatite -HA were also dispersed in DMSO solvent, but at room temperature and stirred until evenly distributed or dissolved. Finally, all the components are mixed and poured onto the base, and the film is formed with forming rods and dried in an oven at 60 °C for 5-6 hours. In Figure 1, you can see the whole preparation process.

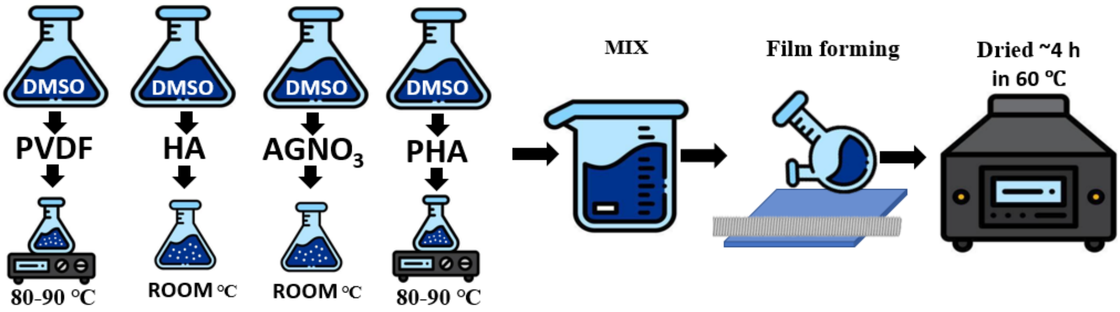

Fig. 1: Solvent casting process.

2.2. Results

Four different films were prepared for the study. Concentrations and compositions are submitted in Table 1.

Tab. 1: Specimens and concentrations.

Sample	PVDF	PHA	$AgNo_3$	HA
1	0,5g/2ml DMSO	-	-	0,05g/1ml DMSO
2	0,5g/2ml DMSO	-	-	-
3	0.3g/2ml DMSO	0.05g/1ml DMSO		
4	0.5g/2ml DMSO	0.1g/1ml DMSO	0.2/1ml DMSO	0.02g/1ml DMSO

Figure 2 shows the average angles between the water drop and the spin-coated samples on a hard film. Mean angle values (θ Young) ranged from 46.7° to 66.29°, and the smallest angle belonged to the spin-coated sample 4 on the film. Good irrigation can be again shifted based on $\theta < 90°$ for all samples. Sample 4 was shown to have a better liquid match than the other samples.

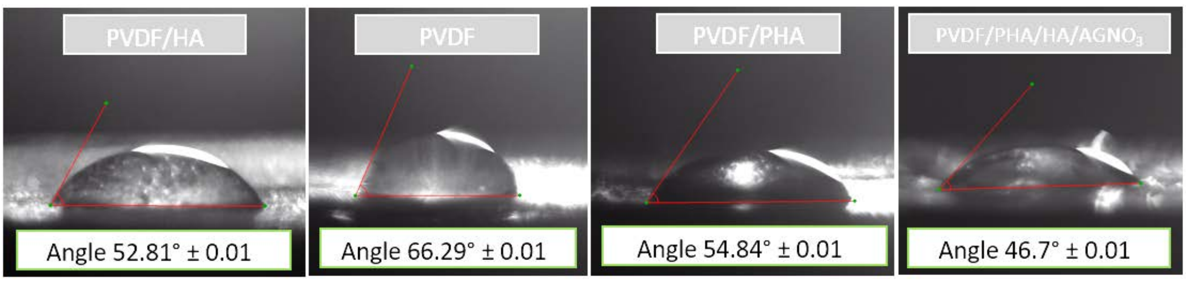

Fig. 2: Hydrophilic angles of samples.

Str (texture aspect ratio) parameter is a measure of surface texture uniformity. The value is obtained by dividing the horizontal distance in the direction in which the autocorrelation function decreases to the value [s] by the horizontal distance in the direction of slowest decrease. In image processing, the autocorrelation function is a measure of the correspondence between an image presented at different coordinates and the original image. The autocorrelation function is calculated by:

$$f_{ACF}(t_{x^0} t_x) = \frac{\iint_A z(x,y) z(t_{x^0} y - t_y) dxdy}{\iint_A z(x,y) z(x,y) dxdy}. \quad (1)$$

Used program: VR-5000 series Viewer Software – [3D measure], Keyence VR series ONE-SHOT 3D, and get the results of surface roughness in Figure 4. There we can see in functional element added HA we get higher surface roughness level.

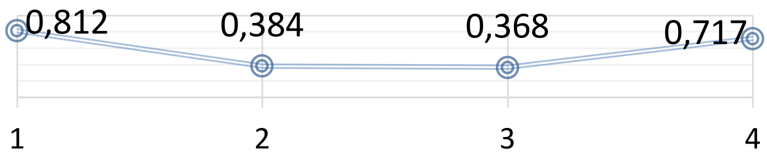

Fig. 3: Str -texture aspect ratio.

3. Conclusions

The materials PVDF - polyvinylidene fluoride, HA - hydroxyapatite, PHA -polyhydroxyalkanoates and $AgNo_3$ - silver nitrate have properties very suitable for a biosensor. Due to its well-known excellent ferroelectric characteristics and biocompatibility, PVDF polymer was chosen to develop the functional element. Additionally, PHA, silver nitrate, and hydroxyapatite were selected for their suitable properties for biosensors and innovation. Silver nitrate has antimicrobial properties. PHAs are biocompatible, biodegradable, and exhibit piezoelectric and nonlinear optical properties. These materials were chosen when creating a functional element - a film. The non-toxic solvent DMSO - dimethyl sulfoxide and the solvent casting method for preparing the thin film were chosen for the preparation of the film.

The hydrophilicity of the samples was investigated and θ Young was determined in the range from 46.7° to 66.29°, and was the lowest value belonging to sample 4. Surface roughness in functional element where added HA got higher surface roughness level.

References

Shanta Pokhel (2018) Advances in Chemical Engineering and Science. Journal of Scientific Research Publishing, 2018, 8, pp. 225-240

Fabricio C. de Paula-Elias, Carolina B.C. de Paula, Nayra M. L. de Oliveira, Alex F. de Almeida, Jonas Contiero (2021) Chapter 1 - Polyhydroxyalkanoates: naturally occurring microbial polymers suitable for nanotechnology applications. Journal of Handbook of Greener Synthesis of Nanomaterials and Compounds. Publishing Volume 2: Synthesis At the Macroscale and Nanoscale 2021, pp. 3-20

Soroush Dashtizad, Parvin Alizadeh, Armin Yourdkhani (2021) Improving piezoelectric properties of PVDF fibers by compositing with BaTiO3-Ag particles prepared by sol-gel method and photochemical reaction. Jourbnal of Alloys and Compounds. Publishing Volume 883, 25 November 2021, 160810

Martin Koller (2020) Advances in Polyhydroxyalkanoate (PHA) Production, Volume 2. MDPI book Bioengineering, Publishing 2019, 6, 108, pp. 175-185

S. Vanaei, M. S. Parizi, F. Salemizadehparizi, H. R. Vanaei (2021) An Overview on Materials and Techniques in 3D Bioprinting Toward Biomedical Application, Journal of Sciense Direct, Publishing Engineered Regeneration Volume 2, 2021, Pages 1-18

S. Satapathy, Santosh Pawar, P. K. Gupta, K. B. R. Varma (2011) Effect of annealing on phase transition in poly(vinylidene fluoride) films prepared using polar solvent. Journal of Indian Academy of Sciences. Published Bull. Mater. Sci., Vol. 34, No. 4, July 2011, pp. 727–733.

Rutika Sehgal, Reena Gupta (2020) Polyhydroxyalkanoate and its efficient production: an eco-friendly approach towards development. Journal of Springer 3 Biotech. Publishing 3 Biotech volume 10, Article number: 549 (2020).

Ans Al Rashid, Shoukat Alim Khan, Sami G. Al-Ghamdi, Muammer Koç (2021) Additive manufacturing of polymer nanocomposites: Needs and challenges in materials, processes, and applications. Journal of Materials Research and Technology. Publishing Volume 14, September–October 2021, pp. 910-941

A. A. Ribeiro, L. G. Vaz, A. C. Guastaldi, J. S. C. Campos (2012) Adhesion strength characterization of PVDF/HA coating on cp Ti surface modified by laser beam irradiation. Journal of Elvesier, Applied Surface Science. Publishing Volume 258, Issue 24, 1 October 2012, pp. 10110-10114

Xiongjie Li, Yiping Wang, Tingrui He, Querui HU, Ying Yang (2019) Preparation of PVDF flexible piezoelectric film with high β-phase content by matching solvent dipole moment and crystallization temperature. Journal of Journal of Materials Science: Materials in Electronics. Publishing 30, pp. 20174–20180 (2019)

Andrey Smirnov Svyatoslav Chugunov Anastasia Kholodkova Maxim Isachenkov, Alexander Vasin, Igor Shishhovsky (2021) Progress and challenges of 3D-printing technologies in the manufacturing of piezoceramics. Journal of Ceramics International. Publishing Volume 47, Issue 8, 15 April 2021, pp. 10478-10511