Original Article

Synthesis, Characterization and Study on Enhanced Hydrophobicity of Novel PVC-MoS2 Composites for Biomedical Applications

M. Subitha1* , B. Bindhu2
[1,2]Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Thuckalay, Tamilnadu, India.
Email: mahesubi2014@gmail.com*

Abstract

This study focus on the synthesis and characterize PVC films containing different concentration of Molybdenum Disulphide (MoS2) filler material prepared by adopting the casting method. The addition of a low molecular weight modifier to PVC makes it a better biocompatible hydrophobic material. This study considers the hydrophobic surface characteristics and in turn the haemolysis prevention associated with it. Based on the physical analysis of water uptake (Wettability) study investigation, an increase in the amount of MoS2 material showed an increase in surface hydrophobicity of PVC- MoS2 composite films. Thus, bio-evaluation of MoS2-PVC films showed that the material is free of haemolysis. From the results, it can be concluded that the prepared composites possess increased hydrophobic behavior which makes them suitable for biomedical applications.

Keywords: Polyvinyl Chloride (PVC), Molybdenum Disulphide (MoS2), Hemocompatibility, Surface modification.

DOI: 10.47750/pnr.2022.13.S03.169

Introduction

Polyvinyl Chloride (PVC-an organic polymerized substance) bags which are soft and flexible were the best alternative found to be used instead of traditional glass bottles due to their properties like heat resistance, durability, low cost, high performance, and inertness. Research is trying to develop and replace traditional methods and materials with newer advancements. PVC is generally hydrophobic, flexible, and unbreakable. Because of the hydrophobic nature of the surface of the polymer, PVC confronts several problems. According to contemporary thinking, surface hydrophobicity can have serious repercussions, especially when substances are exposed to the biological system. This has prompted a lot of studies in recent years to find effective ways to solve the problem. Study [1] used ozone to modify the exterior of PVC and discovered that the substitution of chlorine with oxygen-containing compounds led to a rise in selective hydrophilicity.

It was fascinating to see that ozonation resulted in decreased roughness, which was defined as a component that contributed to an elevation in hydrophilicity.

The research work [2] discovered that chemical gas treatment of the interfaces of PVC film with phosphorus and vanadium-containing units made polymers' surface layer more hydrophilic, while titanium- and silicon-containing groups made the surface layer more hydrophobic. PVC Surface Modification is primarily used for several purposes. It has previously been used to imbue PVC with biological activity, ink processability, and ion penetration.

Molybdenum disulfide (MoS2) is a layered 2-dimensional material similar to graphene in terms of semiconductor and diamagnetic properties. Due to its several good qualities, it has drawn much investigation in the domains of electrochemistry, composite compounds, lubrication, and photochemistry [3]. Physical features include high carrier motility, photoconductivity, sensitivity, as well as mechanical- physical qualities. These characteristics make the MoS2 nanosheet an attractive choice for a wider range of applications, including batteries, transistors, light detectors, and electrical and mechanical devices.

The peculiar wetting response of MoS2 compounds, which is comparable to that of graphene, has recently been observed. To the best of our knowledge, no publications on PVC- MoS2 films with increased hydrophobic activity suited for blood bag methods had been applied, according to literature. As a result, the objectives of this study are to produce PVC- MoS2 composites and to verify their appropriateness for blood bag application.

Materials And Methods

Molybdenum disulfide (MoS2, 99% pure) (Sigma Aldrich) with molecular weight (MW) - 160.06g/mol of AR grade, Lithium hydroxide (Sigma Aldrich) having M.W of 41.96 g/mol, and Dimethylformamide (Thermo fishers scientific) (DMF, purity ≥ 99.9%), Polyvinyl Chloride (PVC) (Thermo Scientific), Stearic acid (Invitrogen) molecular weight (M.W., 284.49 g/mol) were used in the present work.

The plasticized membranes of PVC were prepared by casting method. At first, 0.5gm of PVC was dissolved in 50 ml of DMF. Nanosheets of MoS2 were prepared through the well-known exfoliation technique [4]. MoS2 nanoflakes were modified using Lithium Stearate. These modified MoS2 nanoflakes were added to the PVC solution and stirred using a magnetic stirrer. After 30 minutes of stirring, the PVC-MoS2 solution was cast onto a tidy Petri dish evenly and cast at 37º C. After a day, the casted film was removed and stored. Five different plasticized films viz., PVC film cast as such, PVC-exfoliated and unmodified MoS2 films, PVC-Lithium Stearate Modified MoS2 films at 1w%, 2w%, and 3w% were prepared. The respective casted films were coded as PVC-M0, PVC-M1, PVC-M2, PVC-M3, and PVC-M4 accordingly. Figure 1(a) shows an image of surface-modified MoS2 samples.

Results And Discussions

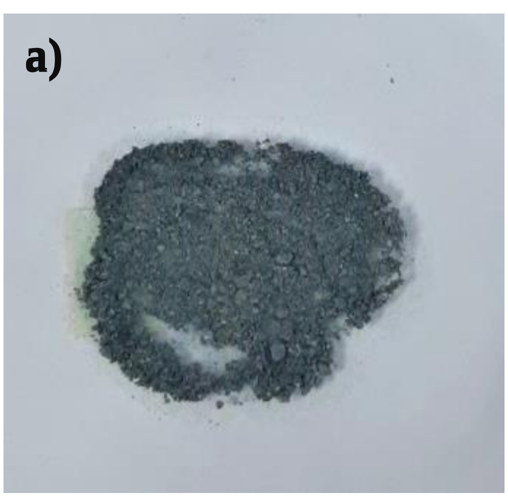
The following characterizations are done to check the hydrophobicity of synthesized samples.

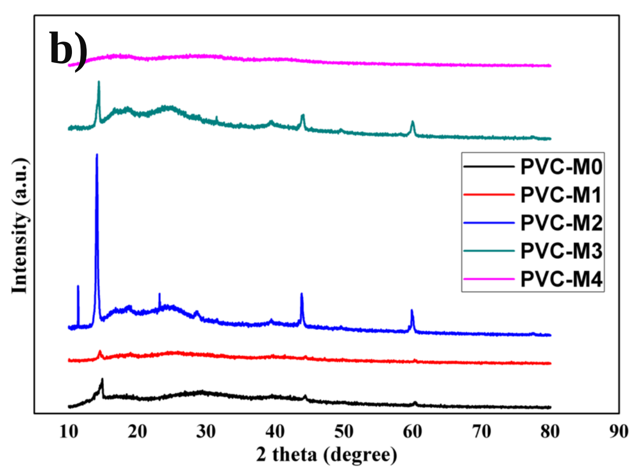
Xrd Analysis

The XRD analysis of the powdered sample is carried out using the XPERT-PRO X-ray diffractometer with the CuKα radiation(λ=1.5406Ao) operating at 30mA and 40 kV. The spectra of the four samples (PVC-M1, PVC-M2, PVC-M3, and PVC-M4) were obtained and are shown in figure 1(b). From the graph, a strong peak at (002) indicates samples are in the crystalline structure. All the reflections are in good agreement with the hexagonal structure. The interlayer separation for the d(002) is higher for the sample PVC-M2 when compared to PVC-M1 & PVC-M3. This signifies better exfoliation for PVC-M2, it is a finely exfoliated sample without destroying its finely crystalline structure.

Tga Analysis

The TGA results were obtained from the TA instrument (Q50) V20.13) (USA). The samples were analyzed in the nitrogen atmosphere at a scan rate of 10oC/min in the programmed temperature range of 800oC.





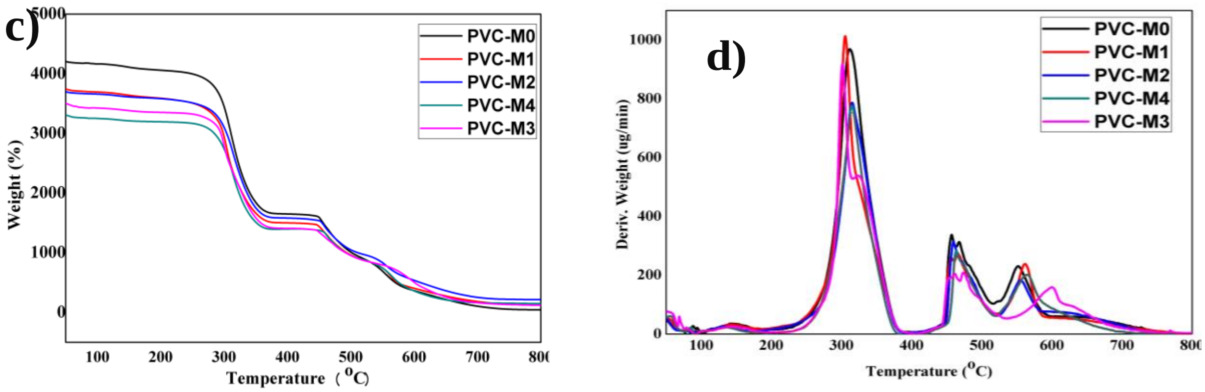


Fig.1: (a). Surface modified MoS2 samples, (b) TGA curves of prepared PVC-MoS2 samples, (c) DTG curves of prepared PVC-MoS2 samples, and (d) TGA curves of prepared PVC-MoS2 samples.

The derivative peak temperature is used as the maximum temperature which is acquired from the differentiation of weight change that is the function of time. The obtained graphs of the samples are given below. Thermogravimetric graph of the PVC-M4 and the prepared samples (PVC-M1, PVC-M2, and PVC-M3) are obtained and they are indicated in figure 1(c) from the spectra of PVC-M4, it is evident that weight loss occurred at 429oC. It is due to the oxidation of molybdenum disulfide to MoO3 [5]. The first stage of weight loss is attributed to the DMF content. Then, the sample is stable between 214oC and 411oc. Thereafter, a small reduction in mass and weight percentage is noticed and this is due to the dehydration of benzyl benzoate.

Hemocompatibility

Hemocompatibility tests were performed for the utility of the prepared materials in some medical devices [6]. Anticoagulant blood was used in this study. Initially1ml of anticoagulant acid, Ethyl Diamine Tetra Acetic Acid (EDTA) was added to fresh blood (9ml). Before performing the test, MoS2-PVC film (1cm2) of codes PVC-M0, PVC-M1, PVC-M2, PVC-M3, and PVC-M4 all were put in Polypropylene (PP) test tubes and7ml of PBS of PH 7.0 was added. These tubes were kept inside the incubator at 37ºC. After 72hrs, the PBS was removed from the sample. Then 1ml of EDTA blood was added to each sample. These samples were kept at 37ºC for 3hrs. The % of haemolysis is found by the equation 1.

$$\% \ of \ \ Hemolysis = \frac{A \ test \ sample \ - \ A(-) \ control}{A(+) \ control \ - \ A(-) \ control}$$

(1)

Figure 2(a) shows the haemolysis % of prepared samples. The material can be classified into 3 categories defined as the haemolytic index (haemolysis %): The percentage of haemolysis above 5% is considered haemolytic; the haemolytic index between five and two percent is considered slightly haemolytic. When the haemolytic index is below two percent, it then comes under non-haemolytic material [7]. All the MoS2-PVC film's haemolytic indexes were found to be below two percentage haemolytic index. So, PVC-MoS2 film has non-hemolytic properties.

Thrombogenicity

PVC-MoS2 film (1cm2) with codes PVC-M0, PVC-M1, PVC-M2, PVC-M3, and PVC-M4 were placed in PBS at a constant temperature, room temperature. After two days, the PBS was removed from the samples. EDTA blood was coated with the surface of the samples. Each of the samples was placed in the Petri dish and also coated with the EDTA blood the Petri dish, which was a + ve control. The blood clotting test starts by adding a 0.01ml solution of calcium chloride. After forty-five minutes it was added to 5ml water. The resultant blood clot was immersed with 5 ml of 36 percent of formaldehyde solution. These solutions with help of tissue paper were dried and finally, the thrombus weight was measured.

The above figure 2(b) shows the thrombus weight obtained on the thrombogenicity test. This property is related to the hydrophilicity of the material. When in contact with a hydrophobic surface, proteins adsorbed strongly and in an irreversible way, then the hydrophilic surface proteins adsorb weakly and in a reversible way [8]. The relation between thrombosis and hydrophilicity was confirmed by an increase in the thrombus weight which was the result of an increment in hydrophobicity. When observed the blood was contacted with the PVC-MoS2 film, it was found that the thrombus weight got increased.

Water Uptake

The hydrophobic behavior of MoS2 prevents the adsorption of the water molecule to plasticized PVC films [9]. Figure 2(c) shows depict PVC-MoS2 film on water uptake. A rise in water absorption can be noticed in the graph. The hydrophobic nature of MoS2 blocks water molecules from adsorbing to modified PVC membrane [10]. The structural variations and quantity of adsorbed proteins have a crucial influence on wettability. The significance of hydrophobic interaction showing the rise in adsorbed protein with reduced wettability of surface can be noted that is, the usual rule of hydrophobic nature. This hydrophobic behavior was mostly suitable for MoS2-PVC films, which confirmed the physical analysis of the water uptake test.

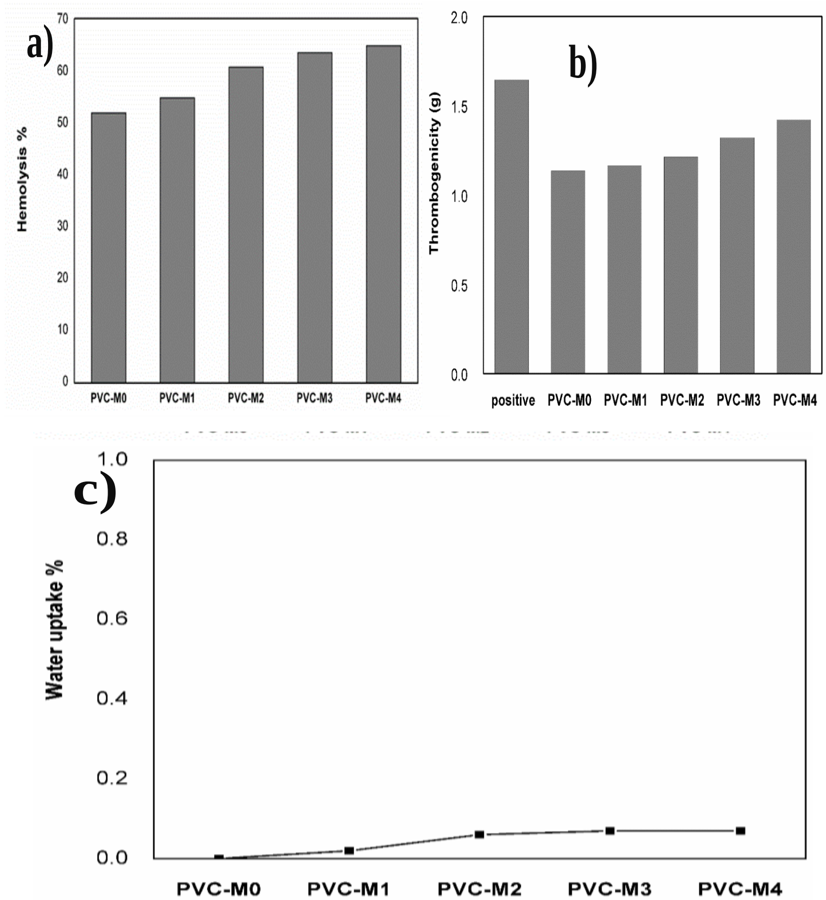


Fig.2:- Haemolysis % of pure PVC and that modified with different amounts of MoS2. 2(b) Thrombogenicity of pure PVC and that modified with Various amounts of MoS2 and 2(c) Water uptake pure PVC and modified with different amounts of MoS2

Conclusions

Plasticized PVC films modified with MoS2 nanosheets were synthesized in this work. With rising MoS2 concentrations, we can observe an enhanced hydrophobic performance of the composites samples. The haemolysis test results indicate that the MoS2-PVC film's haemolytic index was found to be below two percent. So, PVC-MoS2 film has non-haemolytic properties and better biocompatible material having increased hydrophobicity of the surface. The hydrophobic behavior of PVC- MoS2 films were improved, according to the examination of formed films by hydrophobic experiments. The hydrophobic behavior validated the hemocompatibility and thrombogenicity bio-evaluation approach. The results of the above investigations show that PVC- MoS2 films are an excellent hydrophobic material, which in turn states that it can be utilized in biomedical applications.

References

Kurose, K., Okuda, T., Nakai, S., Tsai, T. Y., Nishijima, W., & Okada, M. (2008). Hydrophilization of polyvinyl chloride surface by ozonation. Surface Review and Letters, 15(06), 711-715.

Okuda, T., Kurose, K., Nishijima, W., & Okada, M. (2007). Separation of polyvinyl chloride from the plastic mixture by froth flotation after surface modification with ozone. Ozone: Science and Engineering, 29(5), 373-377.

Tickner, J. A., Schettler, T., Guidotti, T., McCally, M., & Rossi, M. (2001). Health risks posed by the use of Di-2-Ethylhexyl phthalate (DEHP) in PVC medical devices: A critical review. American journal of industrial medicine, 39(1), 100-111.

Xing, Y., Wu, Z., Yang, J., Wang, X., & Liu, L. (2020). LIPSS combined with ALD MoS2 nano-coatings for enhancing surface friction and hydrophobic performances. Surface and Coatings Technology, 385, 125396.

Wen, X. Q., Liu, X. H., & Liu, G. S. (2010). Improvement in the hydrophilic property of the inner surface of polyvinyl chloride tube by DC glow discharge plasma. Vacuum, 85(3), 406-410.

Subitha, M., Sasikanth, S. M., & Bindhu, B. (2019, April). Ionic liquid assisted exfoliation and dispersion of molybdenum disulfide: Synthesis and characterization. In AIP Conference Proceedings (Vol. 2100, No. 1, p. 020098). AIP Publishing LLC.

Larsson, L., Sandgren, P., Ohlsson, S., Derving, J., Friis-Christensen, T., Daggert, F., & Uhlin, M. (2021). Non-phthalate plasticizer DEHT preserves adequate blood component quality during storage in PVC blood bags. Vox Sanguinis, 116(1), 60-70.

Ding, X., Fan, G., Huang, Y., & Wang, J. (2021). Preparation and characterization of an effective microwave absorbent: RGO-MoS2-Fe3O4 nanocomposite. Journal of Materials Science: Materials in Electronics, 32(7), 9640-9649.

Lenz-Habijan, T., Brodde, M., Kehrel, B. E., Bannewitz, C., Gromann, K., Bhogal, P. & Henkes, H. (2020). Comparison of the thrombogenicity of a bare and anti-thrombogenic coated flow diverter in an in the vitro flow model. Cardiovascular and interventional radiology, 43(1), 140-146.

Imai, Y., & Nose, Y. (1972). A new method for evaluation of antithrombogenicity of materials. Journal of biomedical materials research, 6(3), 165-172.