Nano World Journal

https://doi.org/10.17756/nwj.2022-s1-013

Research Article

Open Access

Structural and Morphological Properties of Polyvinylidene Fluoride/reduced Graphene Oxide Nanocomposites

Priyanka Kumari[1], Vishakha Sharma[1], Arpana Pal Sharma[2], Kamakhya Prakash Misra[2], Sanjib Kabi[3], Susruta Samanta[1], Saikat Chattopadhyay[2], and Uvais Valiyaneerilakkal[2*]

[1]Department of Chemistry, School of Basic Sciences, Manipal University Jaipur, Jaipur, Rajasthan, India

[2]Department of Physics, School of Basic Sciences, Manipal University Jaipur, Jaipur, Rajasthan, India

[3]Department of Physics, Sikkim Manipal Institute of Technology, Sikkim Manipal University, Sikkim, India

***Correspondence to:**
Uvais Valiyaneerilakkal
Department of Physics, School of Basic Sciences, Manipal University Jaipur, Jaipur, Rajasthan, India
E-mail: uvaishum@gmail.com

Received: August 23, 2022
Accepted: October 15, 2022
Published: October 17, 2022

Citation: Kumari P, Sharma V, Sharma AP, Misra KP, Kabi S, et al. 2022 Structural and Morphological Properties of Polyvinylidene Fluoride/reduced Graphene Oxide Nanocomposites. *NanoWorld J* 8(S1): S64-S68.

Published by United Scientific Group

Abstract

Single layer graphite, popularly known as graphene, has attracted much scientific interest in recent years due to its outstanding mechanical, thermal, and electrical properties. Recent research confirms graphene is ideal as a nano filler to improve physical and chemical properties of polymers. In this study, we aim to understand the structural and morphological properties and their modifications occurring during nanocomposite fabrication. Polyvinylidene fluoride/reduced graphene oxide (PVDF/rGO) based polymer nanocomposites were prepared by adding various concentrations (2% and 5%) of rGO into the PVDF polymer matrix. At first the liquid phase of the polymer composite was prepared using bath sonication process, then it was converted to film by annealing at 120 °C for 2 hrs. Annealing converts the polymer matrix into β-phase. Several characterizations such as XRD, FT-IR, FESEM, and EDS have been employed to confirm the enhancement of β-phase in PVDF by addition of rGO in the synthesized samples. The signature peaks in FT-IR confirm the transition of phase of PVDF from γ to β. FESEM analysis displays some pin-hole formation on addition of rGO, which may be an interesting feature to explore. Elemental mapping by EDS shows approximately an equal distribution of elements in the polymer composites.

Keywords

Polyvinylidene fluoride, Graphene oxide, Nanocomposite, X-ray diffraction

Introduction

Potential applications of polymer composite based materials in various areas of sciences, engineering and medical have prompted intense study in this field. PVDF is one of the most researched polymer structures since its recognition. PVDF has many advantages like its lightweight, flexibility, biocompatibility, and low acoustic and mechanical impedance [1]. It has been established with experimental facts that PVDF can exhibit piezoelectric, ferroelectric, and pyroelectric features in favorable environment. It is attracting greater scientific and engineering interest due to its previously mentioned properties with the development of modern electronic industries. Polymer modification, by addition of nanofillers into it will produce materials with tunable desired properties. Hence it finds fruitful application in various disciplines of sciences like, in high purity semiconductor industry, electronic display device, electronic panel, architectural coating, chemical industry, biomedical membrane, artificial layers, battery, and sensor applications [1-7]. The high aspect ratio to the large surface area of such polymers, causes due to the addition of external nanofiller particles, helps and

to trigger its mechanical and electrical properties to a large extend while compared with similar other micro-sized systems [5-10]. The improved properties and high-performance of the nanocomposites may be mainly due to the high aspect ratio or the high surface area of the nanofillers. PVDF commonly exists in four different phases, namely α, β, γ, and δ. Among them β-phase of PVDF has attracted much interest to the scientific community as it is popularly known to have highest ferroelectric and piezoelectric characteristics while comparing with other phases. At room temperature PVDF commonly shows its α-phase and heat treatment is the most frequently used technique to convert non-polar α-phase of PVDF to a polar β-phase. The β-phase has significant and spontaneous polarization along the b-axis which is parallel to C-F dipole moment, and perpendicular to the c-axis, of polymer chain direction [11]. The ferroelectric β-phase of PVDF can be achieved either by annealing process or by stretching followed by polling. The differences in electronegativity of fluorine, carbon and hydrogen; electron density is greatest in the vicinity of fluorine atoms which results in such polarization [7, 8] and it may be considered as one of the reasons behind the enhancement of the properties in β-phase. Graphene is a two-dimensional (2-D) material made of a basal monolayer of sp^2 hybridized carbon atoms disposed in a hexagonal packing which now a days are becoming most popular and crucial for a wide range of applications like opto-electronic devices, sensors, biomaterials, energy storage etc [12]. Recently, Graphene and reduced rGO have been used as nanofillers in natural or synthetic polymers to prepare nanocomposites which may be useful in flexible electronics, bioelectronics, bone tissue engineering, developing antibacterial materials, drug delivery, and cancer treatment [13].

Here in this study, we explain the preparation of PVDF/rGO nanocomposites with different rGO amount via chemical route. β-phase of prepared PVDF sample was confirmed using X-Ray Diffraction (XRD) analysis and Fourier transform infrared spectroscopy (FT-IR) study. Field Emission Scanning Electron Microscopic (FESEM) study confirms the surface morphology of the sample. Interestingly, FESEM images exhibit pinhole like structures in the samples.

Materials and Methods

Sample preparation

The process of the synthesis of GO and reduced rGO was explained in detail in our previous study [5, 7]. Initially, a fixed amount of PVDF was added in dimethyl sulfoxide (DMSO) solution and sonicated for 1 hr. Then two different concentrations of rGO (2% and 5%, in wt% ratio w.r.t. polymer weight) were dispersed in the above solution by sonicating for 6 hrs at room temperature. After obtaining proper dispersion of PVDF-rGO solution, it was casted onto a precleaned glass plate. In order to convert the phase of PVDF, the coated films were annealed in a vacuum oven at 120 °C for 2 hrs. Several characterizations such as XRD, FT-IR, FESEM, and EDS have been employed to confirm the enhancement of β-phase in PVDF by addition of rGO in the synthesized samples. A simple schematic is added to understand the process better (Figure 1).

Results and Discussion

X-Ray diffraction

PVDF exists in four different phases, namely α, β, γ, and δ form, among them β-phase of PVDF has attracted much interest, out of which α and β-phase occur majorly, and γ-phase is observed less frequently. To obtain information of crystallite phases XRD measurement was performed. Figure 2 shows the XRD analysis for the samples. XRD pattern of pure PVDF shows crystallite peak at diffraction angle 2θ of 18.61° and 38.88° corresponding to the crystal plane (020) and (002), respectively. These peaks suggest the presence of α-phase of PVDF. The peaks obtained at 2θ = 20.19° for diffraction plane (110) confirms the presence of β-phase. Therefore, through this data it can be concluded that pure PVDF was present in our sample as a mixture of both α and β-phase. In PVDF/rGO nanocomposite (2% and 5%) diffraction peak at 2θ = 37° corresponding to (031) plane appear along with the reduction in diffraction angle 2θ of 18.61° which clearly shows that α-phase of PVDF is decreasing with a gradual increase of β-phase (110) and (031). It can be stated that β-phase is dependent on rGO content in such nanocomposites. The details of XRD analysis of rGO was explained in our previous report [5, 7]. Calculation of particle size (D in nm) using standard Debye-Scherrer method [14, 15] is presented in Table 1.

Fourier transform infrared

Figure 3 shows the FT-IR spectra of PVDF membrane, PVDF-2% rGO nanocomposite and PVDF- 5% rGO nanocomposite. The peaks from 3000 - 3600 cm^{-1} corresponds to the O-H stretching vibration of carboxyl group and water.

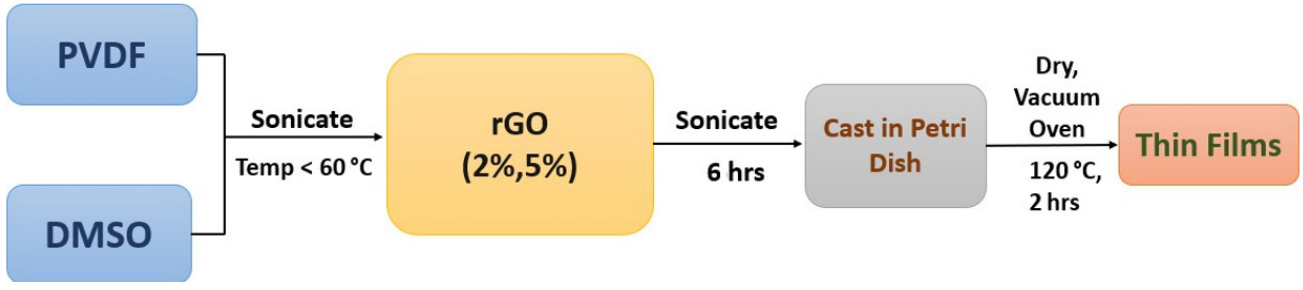

Figure 1: Flow chart of PVDF/rGO nanocomposite synthesis process.

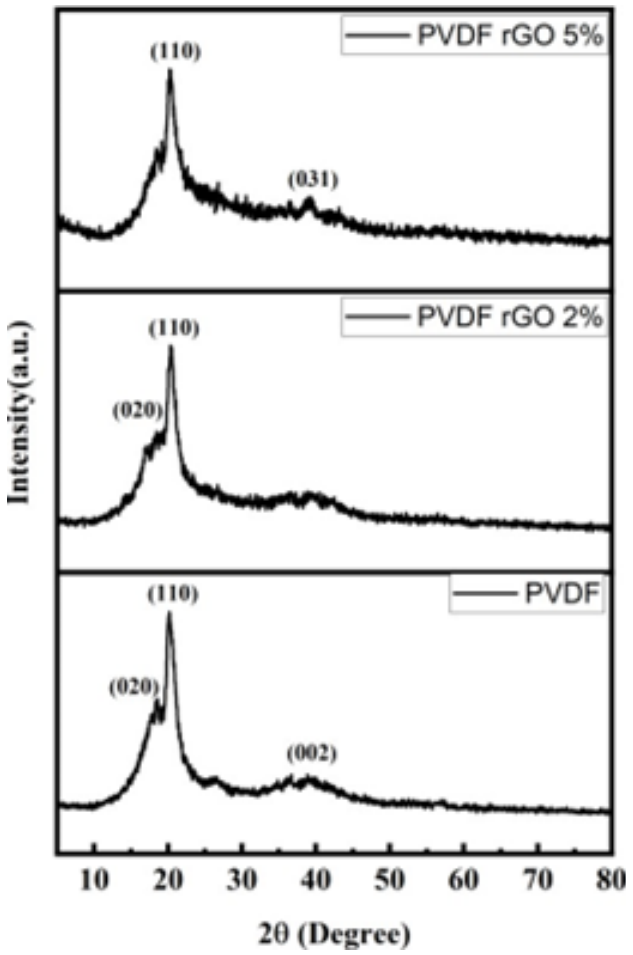

Figure 2: XRD pattern of PVDF and PVDF/rGO nanocomposites.

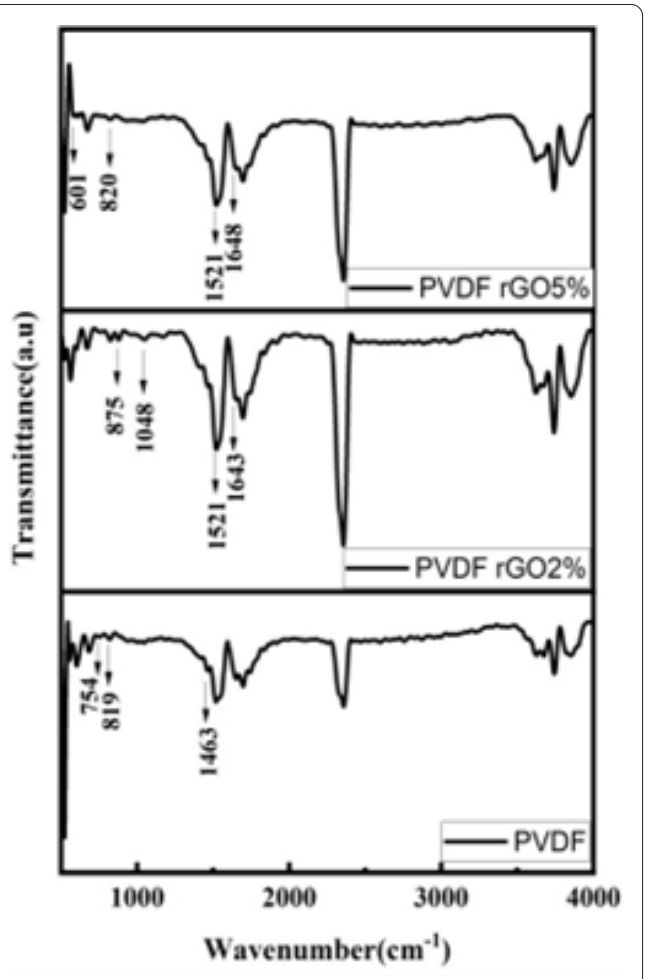

Figure 3: FT-IR spectra of PVDF and PVDF/rGO nanocomposites.

Table 1: particle size calculated from observed X-ray data.

Sample	Peak Position	FWHM	D (in nm)	D Average (in nm)
PVDF	18.61	2.249	3.581	4.370
	20.19	1.564	5.160	
PVDF/rGO (2%)	18.34	1.510	5.330	5.804
	20.34	1.286	6.279	
PVDF/rGO (5%)	18.44	1.505	5.349	5.707
	20.3	1.331	6.064	

Peaks obtained at 1463 cm^{-1} and near to 2500 cm^{-1} contribute to deformation and stretching vibration of C-F and C-H, respectively. Peaks appearing at 1521 cm^{-1} and 1643 cm^{-1} are mainly of rGO and are due to C=C stretching vibration. Peak at 1734 cm^{-1} is due to C=O stretching vibration. The peaks at 608 cm^{-1} and 754 cm^{-1} are assigned to α phase of the PVDF. β-phase of PVDF was confirmed by the peaks obtained at 819 cm^{-1}, 875 cm^{-1}, and 1046 cm^{-1}. In the FTIR of PVDF-rGO nanocomposite the peaks of C-F and C-H diminish to a certain level and peaks obtained due to C=C and C=O stretching exist. A sharp peak approximately at 2500 cm^{-1} is visible due to the presence of carboxyl O–H stretching mode in carbon compound which shows a sharp increase due to incorporation of rGO in different amount. Such observation may be taken as an indirect indication of proper formation of PVDF-rGO composite [16].

Scanning electron microscopy

In order to investigate the topographical variations on PVDF, on addition of rGO, FESEM analysis was done (Figure 4). The microscopic images show that there was not much variation on the topography of PVDF on addition of rGO. This shows that surface microscopic properties of PVDF will not be affected by addition of rGO. Also, the EDS mapping (Figure 5) shows that it was difficult to map the distribution of rGO in PVDF, as both the materials contains carbon.

Conclusion

The impact of rGO on PVDF polymer were analyzed in this work. PVDF being a ferroelectric and piezoelectric material, focus was given to observe the change in corresponding β-phase. β-phase of PVDF was confirmed by the peaks obtained at 819 cm^{-1}, 875 cm^{-1}, and 1046 cm^{-1} from FTIR analysis. In the FTIR of PVDF-rGO nanocomposite the peaks of C-F and C-H diminish to a certain level and peaks obtained due to C=C and C=O stretching exist. The XRD peaks obtained at 2θ = 20.19° for diffraction plane (110) confirms the presence of β phase. FTIR and XRD analysis shows that the ferro-piezo

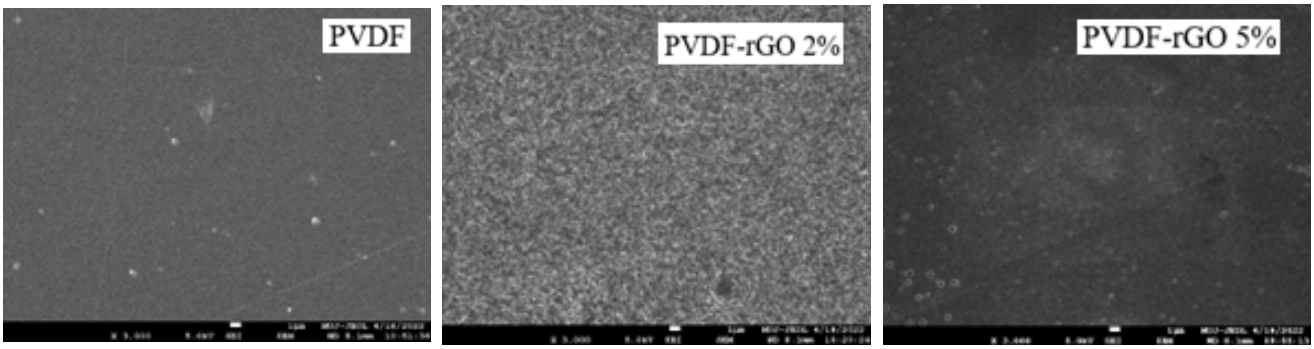

Figure 4: FESEM images of PVDF, PVDF-rGO (2%), and PVDF-rGO (5%) shows that there is not much variation happening on the surface properties of the thin film.

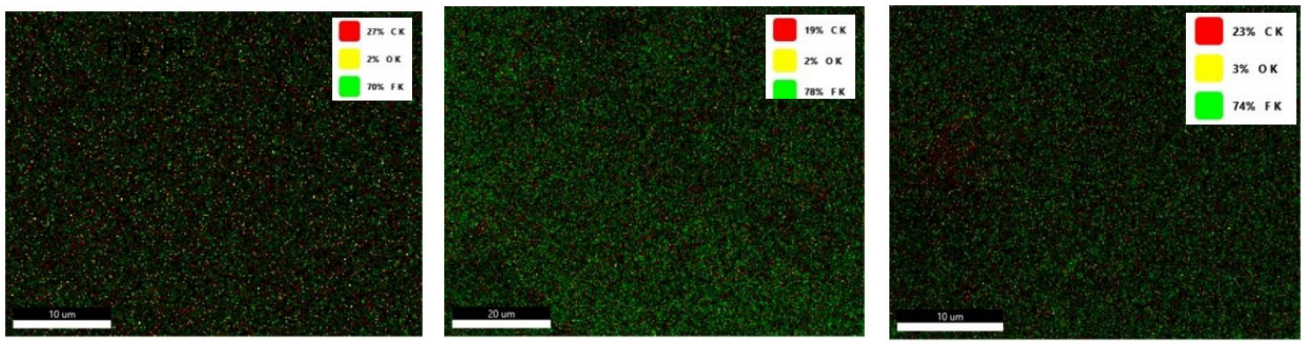

Figure 5: FESEM mapping of PVDF, PVDF-rGO (2%), and PVDF-rGO (5%) shows the distribution of major elements in the thin film.

electric phase was controlled by the concentration of rGO. FESEM images and elemental mapping using EDS shows the surface changes and elemental distribution of PVDF-rGO components.

Acknowledgement

This research was supported by Central Analytical Facilities (CAF) and sophisticated analytical instrument facility (SAIF) at Manipal University Jaipur. We also thank Manipal University Jaipur for awarding Dr Ramdas Pai PhD Scholarship to Ms. Priyanka Kumari.

References

1. Lee H, Wang K, Jee T, Liang H. 2009. Atomic force microscopic study of piezoelectric polymers. In: Bhushan B, Fuchs H (eds) Applied scanning probe methods XIII. NanoScience and Technology. Springer, Berlin, Heidelberg, Germany, pp 137-152. https://doi.org/10.1007/978-3-540-85049-6_6 138-152
2. Xin Y, Sun H, Tian H, Guo C, Li X, et al. 2016. The use of polyvinylidene fluoride (PVDF) films as sensors for vibration measurement: a brief review. *Ferroelectrics* 502(1): 28-42. https://doi.org/10.1080/00150193.2016.1232582
3. Hester JF, Banerjee P, Won YY, Akthakul A, Acar MH, et al. 2002. ATRP of amphiphilic graft copolymers based on pvdf and their use as membrane additives. *Macromolecules* 35(20): 7652-7661. https://doi.org/10.1021/ma0122270
4. De Rosa IM, Sarasini F. 2010. Use of PVDF as acoustic emission sensor for in situ monitoring of mechanical behaviour of glass/epoxy laminates. *Polym Test* 29(6): 749-758. https://doi.org/10.1016/j.polymertesting.2010.04.006
5. Mangavati S, Rao A, Devadiga D, Selvakumar M, Misra KM, et al. 2022. Defects and band gap shrinkage in ZnO/rGO composite nano-pebbles prepared by solid–state reaction. *Diam Relat Mater* 123: 108886. https://doi.org/10.1016/j.diamond.2022.108886
6. Su S, Jiang DD, Wilkie AC. 2002. Methacrylate Modified clays and their polystyrene and poly(methyl methacrylate) nanocomposites. *Poly Adv Technol* 15(5): 225-231. https://doi.org/10.1002/pat.456
7. Mangavati S, Rao A, Devadiga D, Selvakumar M, Saxena M, et al. 2021. Investigation of electrical and thermoelectric properties of zno/rgo composites prepared by conventional solid-state reaction method. *Journal of Nano- and Electronic Physics* 13(1): 01026. https://doi.org/10.21272/jnep.13(1).01026
8. Cha MC, Wu J, Li JX, Cheung KY. 2002. Polypropylene/calcium carbonate nanocomposites. *Polymer* 43(10): 2981-2992. https://doi.org/10.1016/S0032-3861(02)00120-9
9. Pakhira M, Ghosh R, Rath SP, Chatterjee DP, Nandi AK. 2019. Zwitterionic poly(vinylidene fluoride) graft copolymer with unexpected fluorescence property. *Langmuir* 35(16): 5525-5533. https://doi.org/10.1021/acs.langmuir.9b00039
10. El-Masry MM, Ibrahim AS. 2022. Ag-CuO/rGO/PVDF nanocomposite synthesized via simple method as a broadband non-linear optical material for optronic applications. *J Mater Sci Mater Electron* 33: 10851-10865. https://doi.org/10.1007/s10854-022-08066-3
11. Yin Z, Tian B, Zhu Q, Duan C. 2019. Characterization and application of PVDF and its copolymer films prepared by spin-coating and langmuir–blodgett method. *Polymers (Basel)* 11(12): 2033. https://doi.org/10.3390/polym11122033
12. Tarcan R, Todor-Boer O, Petrovai I, Leordean C, Astilean S, et al. 2020. Reduced graphene oxide today. *J Mater Chem C* 8(4): 1198-1224. https://doi.org/10.1039/C9TC04916A
13. Tadyszak K, Wychowaniec JK, Litowczenko J. 2018. Biomedical applications of graphene-based structures. *Nanomaterials* 8(11): 944. https://doi.org/10.3390/nano8110944
14. Kumawat A, Chattopadhyay S, Misra KP, Halder N, Jain SK, et al.

Blue-shift in the optical band gap of sol-gel derived Zn(1-x)SrxO nanoparticles. *Solid State Sci* 108: 106379. https://doi.org/10.1016/j.solidstatesciences.2020.106379

15. Chattopadhyay S, Misra KP, Agarwala S, Rao A, Babu PD. 2019. Correlated quartic variation of band gap and NBE energy in sol-gel derived $Zn_{1-x}Co_xO$ nanoparticles. *Mat Chem Phys* 227: 236-241. https://doi.org/10.1016/j.matchemphys.2019.02.003
16. Emiru TF, Ayele DW. 2017. Controlled synthesis, characterization and reduction of graphene oxide: a convenient method for large scale production. *Egypt J Basic Appl Sci* 4(1): 74-79. https://doi.org/10.1016/j.ejbas.2016.11.002