

Properties and Common Industrial Applications of Polyvinyl fluoride (PVF) and Polyvinylidene fluoride (PVDF)

M. H. Alaaeddin¹, S. M. Sapuan², M.Y.M Zuhri², E.S Zainudin² and Faris M. AL- Oqla²

¹Department of Mechanical and Manufacturing Engineering, UPM, Serdang, Malaysia

²Department of Mechanical Engineering, The Hashemite University, Zarqa, Jordan

E-mails: m.h.alaaeddin@gmail.com; sapuan@upm.edu.my; zuhri@upm.edu.my; edisyam@upm.edu.my; farisv9@yahoo.com

Abstract. This work features the properties and the common industrial applications of two thermoplastic polymers which are the Polyvinyl fluoride (PVF) and the Polyvinylidene fluoride (PVDF), the polymerization and the manufacturing processes of their monomers have been emphasized in this work. It is believed that these two materials are having a number of shared properties and applications. Their distinguishing characteristics allow them to be utilized in various applications with immense interest to the industrial world. They excel, converge, and slightly diverge in most of their properties with diverse transition phases as well as piezoelectric and pyroelectric effects. Their eminent properties qualify them to be used in a number of industrial and outdoor applications e.g. insulations, sensing materials, laminations, encapsulations, coatings, membranes, biomaterials, aircraft interiors and photovoltaic applications. In conclusion, this work recommends further in-depth analysis to investigate the correlations between these two polymers and to provide oriented numerical information on their performance.

1. Introduction

Polyvinyl fluoride (PVF) and polyvinylidene fluoride (PVDF) are considered to be among the closest thermoplastic polymers in terms of their chemical, mechanical and physical properties [1–3]. Both fall under the tree of fluoropolymers which consists of fluorine atoms in the structural formulas [2,4]. The PVF and the PVDF were used competitively in the last few decades due to their distinguished properties and high performance; they have been used in different and similar applications [5,6]. Moreover, the two polymers are believed to share relevant optical, piezoelectric and pyroelectric properties as well as isomorphic characteristics [7]. This convergence in their properties promotes the utilization of these two polymers in certain applications e.g. PVF/PVDF films, hybrid membranes, coatings, encapsulation materials and outdoor applications [8,9]. In addition, possessing piezoelectric and pyroelectric properties widens the use of these polymers to include other sensitive and advanced applications [7,10].

2. PVF And PVDF Structure

PVF is a thermoplastic polymer which contains on a repeating vinyl fluoride (VF) unit, it is comparable in its structure to the PVDF [2]. The chemical formula of PVF is $(C_2H_3F)_n$ with one fluorine atom for two carbon atoms, whereas the PVDF chemical formula is $-(C_2H_2F_2)_n-$ with two fluorine atoms and two carbon atoms [11,12]. However, there has been considerable progress in the



development of copolymers and terpolymers in vinyl fluoride with extra fluorinated monomers e.g. tetrafluoroethylene, hexafluoropropylene, perfluoro-butylethylene [12]. Furthermore, fluoropolymers can be considered as homopolymers and copolymers, the fluorinated fluoropolymers usually encompass the atoms of carbon (C), hydrogen (H) and fluorine (F) or chlorine (Cl). Figure 1 provides ball-and-stick model of PVF and PVDF structure.

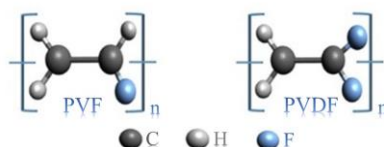


Figure 1. Ball-and-stick model for the structure of the PVF and the PVDF [13]

The PVF and the PVDF are manufactured according to a specific use with varied controllable specifications. These specifications vary according to the functionality and the nature of product [2,11,13]. The two polymers have exhibited high attributes and good mechanical properties, both polymers have been confirmed to have a good tensile strength, although there is a slight difference in favor of the PVF, the PVDF also showed eminent collective properties with strong reliability [1,10,13]. On the other hand, the polyblends between these two polymers have showed different mechanical properties which can be investigated separately [1]. The properties of the PVF and the PVDF can be slightly altered by certain chemical treatments and able to adapt in a homogeneous manner, the modifications can be applied on the mechanical strength, mass transfer, thermal stability, chemical stability, and the degree of crystallinity [3,14]. Table I. provides information on the most common and shared applications of the PVF and the PVDF.

Table 1. A Comparison Of The Most Common Applications Of PVF And PVDF

APPLICATION	PVF	PVDF
Encapsulations	Photovoltaic applications, encapsulation materials and commercial products [4].	Photovoltaic applications, sensing materials and Melt-Bonding Laminations [15,16,17].
Release films & adherent materials	Carbon fiber reinforced polymer composite (CFRP), Fiber reinforced polymer (FRP), peel ply and many relevant applications [18].	Contact surfaces, Piezoelectric materials, peel ply, sealant-adhesives and Products with external protection layers [19,20].
Insulations & interiors	Aircraft parts, Wiring and cabling, sidewalls and stow pin doors, ceiling panels and products with insulation covers [4,10,21].	Premium wire, products with protective barriers, insulation coatings and aircraft interiors [14,22].
Membranes	Hybrid membranes, roofing membranes, antifouling membranes and translucent design elements [8,23].	Nanofibrous membranes, Hybrid membranes, composite membranes, antifouling membranes and super-hydrophobic membranes, micro and ultra-filtration membranes [24-27].

3. Polymerization And Manufacturing Of Vinyl Fluoride and Vinylidene Fluoride

The polymerization process of vinyl fluoride (VF) relies on a number of different techniques, adjutants and initiators, the use of each one of them should be according to the polymerization procedure. The suspension polymerization method uses the technique where the vinyl fluoride is suspended in water, the recommended adjutant for this method is the dispersion stabilizer and the organic peroxide as an initiator. The graft polymerization applies the radiation technique considering the grafting with monomers and the γ -rays. While the radiation-induced method decomposes into free radical. The bulk polymerization technique uses the irradiation with UV method and the Di-tert-butyl peroxide to support the interaction, whereas the emulsion polymerization functions through the procedure of reduced pressure emulsifiers at lower temperatures; the reaction occurs with radical initiators in

aqueous emulsion as preferred [5,10,12,13]. On the other hand, the vinylidene fluoride (VDF) can be polymerized in an aqueous medium in either suspension or emulsion procedures. The polymerization of VDF in nonaqueous mediums and with copolymers in a collection of fluorinated and nonfluorinated monomers have been in a continuous development and research area. However, the emulsion and suspension polymerizations are the most two recommended and commercially practiced procedures. This is due to the sufficient heat sink provided by water for the large heat release. In the VDF emulsion procedure, the water-soluble perfluorinated-emulsifying agent can be applied to prevent radical scavenging reactions in the polymerization process and in order to produce stabilized latex with good solid substance. There are different components and methods to be used in the initiating process of the VDF polymerization e.g. the organic peroxides, the inorganic peroxy compounds, fluoroaliphatic sulfinate and bromates combinations as well as redox methods. Numerous chain-transfer agents can be applied in the polymerization process i.e. the mercaptans, esters, chlorofluorohydrocarbons and fluorohydrocarbons. Nevertheless, the temperature, pressure, polymerization procedures, process structure, monomer feeding strategy and the post-polymerization methods are considered as the variables that directly influence the properties and the final form of the PVDF. The recognized degree of polymerization of PVDF ranges from 1000 to 2500 VDF units in the commercial category. The suspension polymerization procedure can be applied using radical photoinitiators with visible light (UV), the photogeneration reduces the polymerization temperature. Throughout the radical-initiated polymerization process of the VDF, the head-to-tail addition preponderates the structure in the monomer units, the Head is CF₂ and the tail is CH₂, the reversed monomeric addition leads to head-to-head and tail-to-tail structure, which designates the CF₂ CF₂ and CH₂ CH₂ respectively, and this is the point where the defect structure occurs. The rate increases when the polymerization temperature increased which has a significant effect on the degree of crystallinity and the ultimate morphology. Lowering the temperature of the polymerization process reduces the number of defect structures in the PVDF. However, the microemulsion polymerization can be held for the VDF and some specific comonomers in the case where the fluorinated surfactant and the fluorinated oil-in-water microemulsion were introduced in the process [22].

4. PVF And PVDF As Competing Polymers

There are specific polymers that differ partially from PVF in their chemical structure i.e. PVDF, PTFE, PVC, and other relevant fluoropolymers with a semicrystalline component [18,28]. These polymers share distinctive features with each other in some mechanical, chemical, physical, thermal properties as well as piezoelectric and pyroelectric properties [29,30]. However, PVDF has reliable Piezo-pyroelectric coefficients [20,29] and therefore contributes to the heat-generated electricity concept with a wide range of applications [29]. The isomorphic features of the PVF and the PVDF make them more homogeneous as vinyl fluoropolymers [1], these features prioritize them to be used in the applications where their distinctive properties perform better. They are suitable candidates for a good number of applications e.g. encapsulations, release films, coatings, outdoor applications, insulations, photovoltaic applications, aircraft interiors, laminations and membranes [8,14,30]. However, the solubility of PVDF is higher, the PVF is harder to solubilize due to its high polarity and melting temperature which interprets the strength of its monomer-monomer interactions [2]. The two polymers exhibit strong correlation with their morphological structures, the isomorphic blends of the PVF and the PVDF can be maintained with ideal weight proportion and outstanding mechanical properties [1].

5. Properties And Distinguished Features

The PVF and the PVDF are known as semicrystalline polymers with a significant variation that ranges between 20-60% and 35-70% respectively. The transition of PVF is below the melting temperature which is 190 °C, and there are several transition phases at Lower T_g which occurs at -15 to -20 °C and the Upper T_g which can be maintained in the range of 40-50 °C, and another two phases were reported between -80 and 150°C. While the PVDF has four named phases as its density differs from each

polymorph phase, these phases are: α , β , γ , and δ . However, α -PVDF phase is the most common state that displays transitions as: (γ) at -70 °C, (β) at -38 °C, (α'') at -50 °C, (α') at -100 °C [31]. Whereas the polarized β -PVDF is mostly known as a potential polymer with good piezoelectric properties [16].

The PVF exhibits strong mechanical, chemical and general properties e.g. tensile strength, Young's modulus, impact strength, elongation, flexural strength, color stability, weathering performance, melting point, heat deflection temperature and thermal transition temperature [7,8,32]. Whereas the PVDF exhibits high impact strength, hardness, thermal expansion, altered density, higher degree of crystallinity, solubility and high limiting oxygen index. In addition, the PVDF exposes better piezoelectric and pyroelectric coefficients [24,26]. Table II shows the fluorine to carbon ratios, the coefficients of friction and the critical surface tension of the commercial PVF and PVDF.

Table 2. Fluorine To Carbon Ratio, Coefficients Of Friction and Surface Energy Of the Commercial Pvf And Pvdv [32,33]

Fluoropolymers	Monomer	Fluorine to Carbon Ratio	Coefficient of Friction (dynamic)	Critical Surface Tension, dyne/cm
Polyvinyl fluoride (PVF)	$\text{CH}_2=\text{CHF}$	0.5	0.3	28
Polyvinylidene fluoride (PVDF)	$\text{CH}_2=\text{CF}_2$	1	0.3	25

6. piezoelectric and pyroelectric properties

The piezoelectricity effect in materials has been defined as the electric polarization that generated in specific crystalline materials at certain mechanical deformation, and the polarity is subjected to a change according to the changes that occurred in the deformation procedure. However, the piezoelectric materials also retain pyroelectric effect at temperature changes [14]. The PVF is relatively lower than the PVDF in terms of the Piezo/Pyroelectric effect. The dipole moment per-repeat unit in the PVDF is greater than the one in the PVF, and the net moment of trans in the PVF is nearly 20% of that found in the PVDF, whereas the Pyroelectric coefficient of the PVF is about 40% of that found in the PVDF [7]. The PVDF demonstrates unusual piezoelectric and pyroelectric properties, which makes it as one of the most attractive and promising polymers [14,33]. The piezoelectric and pyroelectric properties open new potentials and research prospects in these polymers particularly, and can be employed in advanced and piezoelectric applications, such as nanogenerators, sensors, photonic devices, hydrophones, actuators and transducers [22,34,35]. In addition, numerous observations have categorized the PVDF as a ferroelectric polymer with undetected Curie point. The *Curie point* is the temperature point where the transition phase appears in ferroelectric materials which transform into paraelectric state after surpassing this particular temperature [14]. However, table III provides information about the piezoelectric & the pyroelectric constants of the PVF and the PVDF β -phase as well as δ -phase respectively.

Table 3. The Piezoelectric and the Pyroelectric Constants (D_{31}) Of PVF And PVDF [10]

Polymers	Structure	Piezoelectric Coefficient, pC/N	Piezoelectric Coefficient, $\mu\text{C/K.m}^2$
PVF	$-\text{CH}_2-\text{CFH}-\text{CH}_2-\text{CFH}-$	1	10
PVDF (β -phase)	$-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CFH}-$	20-30	30-40
PVDF (δ -phase)	-	10-17	10-15

However, the stability of these two polymers are noticeably high and can keep performing in a good manner, specially in the most extreme chemical environments, the limiting oxygen index (LOI) in both polymers is observed higher in the PVDF and lower in the PVF due to the large proportion of hydrogen atoms in its chain [36].

7. Conclusions

The two thermoplastic polymers are foreseen to have a good number of common properties which qualify them to be utilized in a wide range of industrial and outdoor applications e.g. commercial products, insulations, encapsulations, sensing materials, coatings, laminations, interiors, outdoor applications, aircraft parts and photovoltaic applications. Substantially, some discrepancy might take place in the categorization of PVF and PVDF properties due to the variances occurred in the applied methods. The PVF have shown a wide range of good and reliable properties e.g. the flexural strength, tensile strength, melting point, heat deflection temperature and thermal transition temperature, whereas the PVDF exhibits better piezoelectric and pyroelectric properties, higher impact strength, hardness, thermal expansion, altered density, higher degree of crystallinity, solubility and higher limiting oxygen index. However, further in-depth researches and oriented numerical information are needed to investigate the correlations and contributions of these two distinctive polymers.

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Reference

- [1] A. K. Gupta, R. Bajpai, and J. M. Keller, "Morphological, crystallization and plasticization studies on isomorphic blends of poly (vinyl fluoride) (PVF) and poly (vinylidene difluoride) (PVDF): Using microhardness, XRD and SEM techniques," *J. Mater. Sci.*, vol. 41, Jun. 2006, pp. 5857–5861, doi: 10.1007/s10853-006-0359-2.
- [2] M. Lora, J. S. Lim, and M. A. Mchugh, "Comparison of the Solubility of PVF and PVDF in Supercritical CH₂F₂ and CO₂ and in CO₂ with Acetone, Dimethyl Ether, and Ethanol," *J. Phys. Chem.*, vol. 103, Mar. 1999, pp. 2818–2822, doi: 10.1021/jp9844462.
- [3] D. M. Brewis, I. Mathieson, I. Sutherland, R. A. Cayless, and R. H. Dahm, "Pretreatment of poly(vinyl fluoride) and poly(vinylidene fluoride) with potassium hydroxide," *Int. J. Adhes. Adhes.*, vol. 16, 1996, pp. 87–95, doi: 10.1016/0143-7496(95)00053-4.
- [4] M. DeBergalis, "Fluoropolymer films in the photovoltaic industry," *Journal of Fluorine Chemistry*, Vol.125, Aug. 2004, PP.1255-1257, doi: doi.org/10.1016/j.jfluchem.2004.05.013.
- [5] S. Ebnesajjad, *Manufacturing of Oriented Polyvinyl Fluoride Film*, 3rd ed., Polyvinyl Fluoride Technol. Appl. PVF, William Andrew, 2012, pp. 117–139.
- [6] G. dong Kang and Y. ming Cao, "Application and modification of poly(vinylidene fluoride) (PVDF) membranes - A review," *J. Memb. Sci.*, vol. 463, Mar. 2014., pp. 145–165, doi: 10.1016/j.memsci.2014.03.055.
- [7] A. S. de Reggi, M. G. Broadhurst, and G. T. Davis, "Effects of poling field and time on pyroelectric coefficient and polarization uniformity in polyvinyl fluoride," *Ferroelectrics*, vol. 33, 1981, pp. 119–125, doi: 10.1080/00150198108008077.
- [8] I. Kaur, V. Kumari, B. Sharma, and N. Gupta, "Characterization and applications of PVF film grafted with binary mixture of methacrylic acid and 4-vinyl pyridine by gamma radiations: Effect of swift heavy ions," *Appl. Radiat. Isot.*, vol. 79, May 2013, pp. 118–130, doi: 10.1016/j.apradiso.2013.05.004.
- [9] Z. Liu, H. Wang, X. Zhang, C. Lv, Z. Zhao, and C. Wang, "Durable and self-healing superhydrophobic polyvinylidene fluoride (PVDF) composite coating with in-situ gas compensation function," *Surf. Coatings Technol.*, vol. 327, Aug. 2017, pp. 18–24, doi: 10.1016/j.surfcoat.2017.08.003.
- [10] S. Ebnesajjad, *Fluoroplastics: Melt Processible Fluoropolymers-The Definitive User's Guide and Data Book*, Vol. 2. William Andrew, 2015.
- [11] S. Huber, M. Moe, N. Schmidbauer, G. Hansen, and D. Herzke, "Emissions from incineration

- of fluoropolymer materials—A literature survey,” Norwegian Institute for Air Research: Kjeller, Norway, 2009.
- [12] S. Ebnesajjad, P. R. Khaladkar, *Fluoropolymer Applications in the Chemical Processing Industries -The Definitive User's Guide and Data Book*, 2nd ed. Vol. 2. William Andrew, 2017.
- [13] S. Ebnesajjad, Introduction to fluoropolymers, In *Applied Plastics Engineering Handbook*, 2nd ed. 2017, pp. 55-71.
- [14] M. Chanda, and S. K. Roy, *Industrial polymers, specialty polymers, and their applications*, Vol. 74. CRC press, 2008.
- [15] N. An, H. Liu, Y. Ding, M. Zhang, and Y. Tang, “Preparation and electroactive properties of a PVDF/nano-TiO₂ composite film,” *Appl. Surf. Sci.*, vol. 257, Feb. 2011, pp. 3831–3835, doi: 10.1016/j.apsusc.2010.12.076.
- [16] G. Melilli, D. Lairez, D. Gorse, E. Garcia-Caurel, A. Peinado, O. Cavani, B. Boizot, and M.C. Clochard “Conservation of the piezoelectric response of PVDF films under irradiation,” *Radiat. Phys. Chem.*, Vol. 142, Mar. 2017, pp. 1–6, doi: 10.1016/j.radphyschem.2017.03.035.
- [17] K. Kim, M. Yoo, K. Ahn, and J. Kim, “Thermal and mechanical properties of AlN / BN- filled PVDF composite for solar cell backsheet application,” *Ceram. Int.*, vol. 41, Jan. 2015, pp. 179–187, doi: 10.1016/j.ceramint.2014.08.056.
- [18] F. Mazille, T. Schoettl, and C. Pulgarin, “Synergistic effect of TiO₂ and iron oxide supported on fluorocarbon films. Part 1: Effect of preparation parameters on photocatalytic degradation of organic pollutant at neutral pH,” *Appl. Catal. B Environ.*, vol. 89, Feb. 2009, pp. 635–644, doi: 10.1016/j.apcatb.2009.01.027.
- [19] E. D. Burnham-Fay, T. Le, J. A. Tarbutton, and J. D. Ellis, “Strain characteristics of additive manufactured polyvinylidene fluoride (PVDF) actuators,” *Sensors Actuators A Phys.*, Oct. 2017, pp.85-92, doi: 10.1016/j.sna.2017.08.053.
- [20] T. Tao, Y. Deng, Z. Liang, B. Liang, Y. Yao, P. Li, S. Lu, and Y. Chen, “Synthesis of porous polyvinylidene fluoride (PVDF) microspheres and their application in lithium sulfur batteries,” *Mater. Lett.*, vol. 188, Oct. 2017, pp. 180–183, doi: 10.1016/j.matlet.2016.11.023.
- [21] S. Ebnesajjad, and A. H. Landrock, *Adhesives technology handbook*, 3rd ed., William Andrew, 2012.
- [22] J. S. Humphrey, R. Amin-Sanayei, *Vinylidene fluoride polymers*, Encyclopedia of polymer science and technology, 2004.
- [23] M. Muti, F. Kuralay, and A. Erdem, “Single-walled carbon nanotubes-polymer modified graphite electrodes for DNA hybridization,” *Colloids and Surfaces B: Biointerfaces*, vol. 91, Mar. 2012, pp. 77–83, doi: 10.1016/j.colsurfb.2011.10.042.
- [24] J. Ji, F. Liu, N. A. Hashim, M. R. M. Abed, and K. Li, “Poly(vinylidene fluoride) (PVDF) membranes for fluid separation,” *React. Funct. Polym.*, vol. 86, Jan. 2015, pp. 134–153, doi: 10.1016/j.reactfunctpolym.2014.09.023.
- [25] C. N. B. Elizalde, S. Al-Gharabli, J. Kujawa, M. Mavukkandy, S. W. Hasan, and H. A. Arafat, “Fabrication of blend polyvinylidene fluoride/chitosan membranes for enhanced flux and fouling resistance,” *Sep. Purif. Technol.*, vol.190, Jan. 2018, pp.68-76, doi:10.1016/j.seppur.2017.08.053.
- [26] F. Liu, N. A. Hashim, Y. Liu, M. R. M. Abed, and K. Li, “Progress in the production and modification of PVDF membranes,” *J. Memb. Sci.*, vol. 375, Jun. 2011, pp. 1–27, doi: 10.1016/j.memsci.2011.03.014.
- [27] D. Ghazanfari, D. Bastani, and S. A. Mousavi, “Preparation and characterization of poly (vinyl chloride) (PVC) based membrane for wastewater treatment,” *J. Water Process Eng.*, vol. 16, Apr. 2017, pp. 98–107, doi: 10.1016/j.jwpe.2016.12.001.
- [28] M. Biron, *Plastics Solutions for Practical Problems*, 2nd ed. Thermoplastics and Thermoplastic Composites, William Andrew Publishing, 2013, pp831-984.
- [29] K. Al Abdullah, M. A. Batal, R. Hamdan, T. Khalil, J. Zaraket, M. Aillerie, and C. Salame,

- “The Enhancement of PVDF Pyroelectricity (Pyroelectric Coefficient and Dipole Moment) by Inclusions,” *Energy Procedia*, vol. 119, Jul. 2017, pp. 545–555, doi: 10.1016/j.egypro.2017.07.074.
- [30] K. J. Geretschlager, G. M. Wallner, and J. Fischer, “Solar Energy Materials & Solar Cells Structure and basic properties of photovoltaic module backsheet films,” *Sol. Energy Mater. Sol. Cells*, vol. 144, Jan. 2016, pp. 451–456, doi: 10.1016/j.solmat.2015.09.060.
- [31] M. Kutz, ed., *Applied plastics engineering handbook: processing and materials*, William Andrew, 2011.
- [32] S. Ebnesajjad, “Manufacturing of Unoriented Polyvinyl Fluoride Films and Coatings,” *Polyvinyl Fluoride Technol. Appl. PVF*, 2012, pp. 141–150, doi: 10.1016/B978-1-4557-7885-0.00006-5.
- [33] S. Ebnesajjad, *Introduction to fluoropolymers: materials, technology and applications*, William Andrew, 2013.
- [34] A. Baji, Y. W. Mai, Q. Li, and Y. Liu, “Nanoscale investigation of ferroelectric properties in electrospun barium titanate/polyvinylidene fluoride composite fibers using piezoresponse force microscopy,” *Compos. Sci. Technol.*, vol. 71, Jul. 2011, pp. 1435–1440, doi: 10.1016/j.compscitech.2011.05.017.
- [35] S. Biswas and S. Bhattacharya, “Effect of Ag nanoparticle embedment on electroactive phase nucleation of PVDF and PVDF-HFP under non-isothermal condition: A comparative study,” *Thermochim. Acta*, vol. 649, Mar. 2017, pp. 69–81, doi: 10.1016/j.tca.2017.01.009.
- [36] R. R. Mather, and R. H. Wardman, *The chemistry of textile fibres*, 2nd ed., R. Soc. Chem: Cambridge, 2015.