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A Brief Review on Nanocomposites based on PVDF with Nanostructured TiO_2 as Filler

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Abstract

Nanocomposites are based on a combination of two or more nanomaterials. Depending on the selection of the constituents forming the composite, the end properties may be tuned as per requirements. Moreover, the combination of organic and inorganic materials can help improve the composite properties a step further, and thus provide exceptional functionalities. Owing to their exceptional mechanical and thermal stability, titania (TiO_2) nanostructures are one of the most commonly used reinforcements. Thus, considerable research has focused on the development and characterization of TiO_2 reinforced composites based on several different polymer matrices. Amongst the matrix materials used in different nanocomposites, Polyvinylidene Fluoride (PVDF) is the choicest matrix because of its stability, ease of processing and good mechanical properties relative to other thermoplastic polymers. This review focuses on recent progress in the incorporation of TiO_2 nanostructures into a PVDF matrix so as to develop nanocomposites having outstanding optical, mechanical and electrical properties. A summary of the diverse potential applications of the PVDF/TiO_2 nanocomposites has also been given.

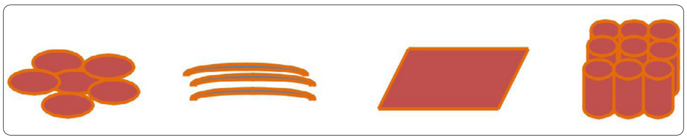
Keywords: Nanocomposites; Polymers; Inorganic nanoparticles; PVDF; TiO_2.

Introduction

Small clusters of atoms from 1 to 100 nanometers long fall under the category of nanoparticles and may be compared to smaller visible living creature - an ant which is millions of nanometers. They are not conformed to absolute quantum chemistry or laws of classical physics and hold strikingly exciting properties in comparison to their bulk counterpart due to increased surface area and quantum confinement effects leading to greater chemical reactivity and enhanced strength [1-5]. Quantum effects become much more important in determining the resultant properties of nanomaterials in terms of unusual electrical, magnetic and optical characteristics [6-8]. Nanoparticles play vital role in broad range of fields for instance pharmaceuticals, electronics and environmental remediation [9-10].

Nanoparticles may be identified as nanocomposites, aerosols, nanopowders, nanoceramics, and colloids contingent to their use of interest. These can include carbon based nanomaterials e.g., fullerenes, nanodiamonds, carbon nanotubes, graphene, metal clusters (Pt, Pd, Au, Ag) and metal oxide nanoparticles like TiO_2, ZnO, Al_2O_3 and SiO_2 biomaterials or organic materials [11]. Out of these different types of nanomaterials, metal oxide nanoparticles have been extensively explored as they are already being utilized in many commercial processes and products. They are widely employed not only as everyday items including paints and varnishes, sunscreens, cosmetics, stain-resistant clothing, sporting goods and electronics but also find applications in the field of nanomedicine as diagnostic, drug delivery and imaging agent [12-15]. Titanium dioxide nanoparticles (TiO_2 NPs) have received utmost interest among other metal oxide NPs owing to its exciting properties for instance cost effectiveness, stability, commercial handiness, exceptional photocatalytic, UV-cleaning, antibacterial properties and biocompatibility [14].

Nano TiO_2 usually exists in different morphological forms for instance either as spherical NPs or as nanotubes. Siegel [16] classified nanostructured materials in general as Zero dimensional (clusters), one dimensional (nanotubes), two dimensional (films) and three dimensional (polycrystalline) nanostructures as represented in figure 1.



Cluster Tubular Films Polycrystalline

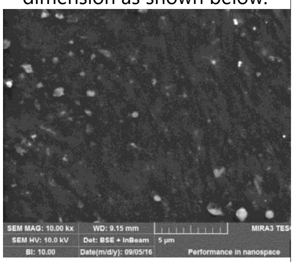
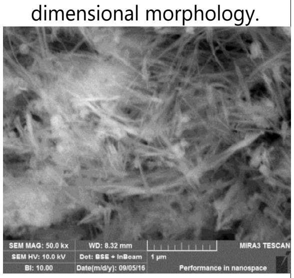
Figure 1. Pictorial representation of different dimensions of NPs.

Properties of the nanoparticles can be exploited for their utilization in various exciting future technologies by controlling their morphology. For instance, nanotubes are preferred in applications including need to create electrical bridges in conducting materials or to store/ process information in magnetic devices [17].

Features of TiO_2- NPs vs Nanotubes

Critical properties of TiO_2 which should be considered for its specific application include geometry, morphology and microstructure. These properties are summarized in Table 1.

Table 1. Properties of TNPs vs TNTs

Properties	TNPs	TNTs
Structure	TiO_2 NPs usually exists in three crystalline forms namely anatase, rutile and brookite. Anatase and rutile phases have tetragonal whereas brookite phase has orthorhombic crystalline structure [18-19].	TNTs exist as anatase phase at/ below 450°C Where as above this temperature converts to rutile phase. However, TNTs deform at elevated temperatures [20].
Morphol-ogy	TNPs are spherical in nature having zero dimension as shown below.  **Figure 2.** SEM image of TNPs	TNTs are tubular in shape having one dimensional morphology.  **Figure 3.** SEM image of TNTs
Synthesis	Most commonly TNPs can be synthesized via following three routes. a) Sol-Gel b) Hydrothermal c) Chemical vapor deposition Apart from these, other synthesis methods for TNPs include solvothermal, direct oxidation, microwave, sonochemical and electrodeposition [21-22].	Following methods are employed for the synthesis of TNTs [22]. a) Sol-Gel b) Hydrothermal followed by alkaline treatment of anatase TiO_2 c) Electrochemical anodization of Ti foil.
Efficiency	NPs of TiO_2 are preferred to get maximum output efficiency for certain application e.g., in photocatalysis, NPs are quite efficient due to enhanced surface area [23].	1-D structures are reported to be more efficient than 0-D NPs due to high surface to volume and aspect ratio. For instance, S. Hernandez et al., has demonstrated that 10 folds enhanced photocatalytic efficiency of TNTs in comparison to TNPs [23].

Nanocomposite of PVDF with TiO_2 nanostructures as nanofiller and applications

Nanoscale innovative material design and synthesis holding unusual properties is important in fabrication of advanced devices for optics, electronics and biotechnology. In this perspective, polymers are considered as a usual choice based on their high surface area and low cost. However the polymeric material lack in mechanical and thermal stability. Thus, in polymer science, there is a dire need to widen the application window by enhancing their mechanical, thermal, and electrical properties. Among the polymeric material, Polyvinylidene fluoride (PVDF) is a semi crystalline polymer posses incredible properties, such as excellent resistance to chemicals, good thermal stability, high mechanical strength and inflammable, etc. Figures 2 and 3 PVDF has been extensively employed in various fields, such as nuclear-waste processing, waste water treatment, pulp and paper industry, chemical processing industry and as piezoelectric material [24-26]. Reinforcement of polymers with incorporation of whisker, platelets, fibers or nanoparticles may be considered as analternative approach to attain improved properties in nanocomposites [27]. Polymer nanocomposites have shown promising ability to maintain balance among customary properties including ease of fabrication and low weight of polymers with the toughness and strength of reinforcing material [28]. TiO_2 is extensively used as filler material for PVDF matrix owing to its promising role in enhancement of mechanical, thermal, electrical and optical properties of PVDF/TiO_2 nanocomposite for potential applications in variety of fields [29-30].

Nanocomposites of PVDF with inclusion of different contents of TiO_2 nanofiller along with their synthesis protocol and applications have been collected in table 1.

Table 2. Nanocomposites based on PVDF/TiO_2

Nanocom-posites	Content of TiO_2	Methods of preparation	Uses	References
PVDF-HFP/TiO_2	<50%		Polymer electrolytes in fuel cells	31
PVDF-HFP/TiO_2	40% rulite		fuel cells	32
PVDF-HFP/ TiO_2c	15%	Phase inversion and conventional casting methods	electrolytes in fuel cells	33
PVDF/LiClO4/ TiO_2	10%	In situ sol–gel process	Polymer electrolytes in lithium ion batteries	34
PVDF-HFP/TiO_2	6.5%	Phase inversion method	fuel cells electrolytes	35
LiDFOB-based PVDF-HFP/TiO_2	5%	Solid state reaction method	Polymer electrolytes in fuel cells	36
PVDF/TiO_2	1.5%	Phase inversion technique	Degeradation of methy blue	37
PVDF/TiO_2/OA	1%	Sol gel	Degeradation Methyl orange	38
PVDF/TiO_2	0–4%	Casting solution	Degeradation of Reactive Black 5	39
PVDF/TiO_2	0.5%	Phase inversion technique	Degeradation of Brilliant Green, Indigo Carmin	40
Poly (vinylidene fluoride) plasma- grafted poly(acrylic acid) membrane/TiO_2	0.5%	Casting solution	Degeradation of Reactive Black 5	41
PVDF	0.5%	sol–gel process and immobilized laccase by chemical coupling on membrane surface	Removal of BPA as high as 90 %	42
PVDF/rGO	0.05%	phase inversion method	Show best fouling resistance	43
PVDF	1-2wt.%	melt-intercalation method	Increase mechanical and tribological properties of membrane	44
PVDF	0.5%	low temperature hydrothermal (LTH) process	membrane distillation	45
PVDF	0.7wt%	Amorphous phase separation	Improved the hydrophilicity	46
PVDF/PEG	0-4%	phase inversion induced by dry-jet spinning method	best adsorption capacity of lead	47
PVDF/PVP	2wt.%		removal of oil	48

L.Yu et al., reported 30% enhancement in tensile strength of PVDF/TiO_2 hollow fibre membranes prepared via blending or method sol-gel [49]. Similarly, an improvement in the tensile strength of PVDF hollow fibre membranes from 1.71 MPa to 3.74 MPa was observed upon incorporation of a combination of 1 wt % Al_2O_3 and 2 wt % TiO_2 in PVDF matrix. The authors attributed this improvement to the formation of compact macro void in the nanocomposite [50]. There is considerable impact of addition TiO_2 on the thermal and electrical properties of PVDF/ HfP as reported by K. Prabakaran et al [51]. They reported about two fold enhancement in the dielectric constant of nanocomposite upon inclusion of surface modified TiO_2 NPs. Moreover, significant changes in optical properties of PVDF could be observed by incorporation of TiO_2.

NPs e.g., Zhang et al and A. Munoz-Bonilla et al have reported the transmittance spectra of PVDF/ ZrO_2-TiO_2 and PVDF/TiO_2 nanocomposite [52-53]. They showed an increase in the absorption and refractive index of the nanocomposite in the presence of TiO_2 NPs. In fact, enhancement in different properties of PVDF/TiO_2 nanocomposite is attributed to the interaction between the filler material and polymer matrix. It has been reported that the fluorine atom of the PVDF polymer can interact strongly with Ti^{4+} ions via Vander Waal forces of interaction to induce mechanical stability to nanocomposites for various exciting applications as shown pictorially in figure 4 [54].

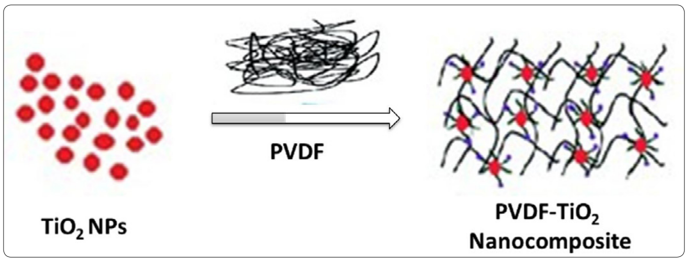


Figure 4. Pictorial representation of formation of PVDF/TiO2 nanocomposite.

The cumulative effect of both PVDF and TiO_2 in nanocomposites is more effective than the individual components. Different combinations of nanocomposites including some other polymer or nanomaterials in the matrix of PVDF have been explored for multiple purposes in various fields of research. Hence, in the following section, different applications of PVDF/ TiO_2 nanocomposites are briefly reviewed (fig 5).

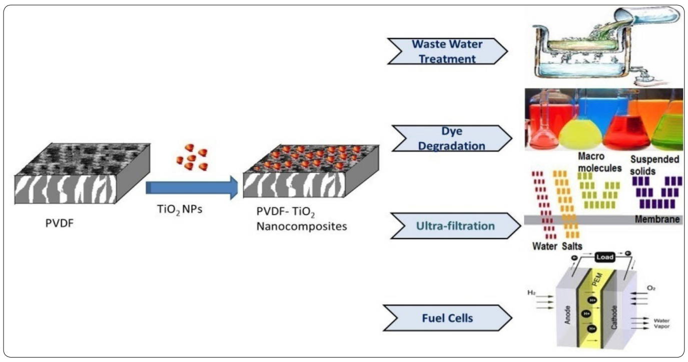


Figure 5. Applications of PVDF/ TiO2 nanocomposite

Environmental application

Extensive reports are available in literature for the utilization of PVDF/ TiO_2 nanocomposite as water treatment membranes, removal of heavy metals and photocatalytic degradation of dyes in textile industry [55]. TiO_2 nanofiller attributes to the enhancement of hydrophilic and antifouling properties of PVDF due to the presence of OH surface groups [56-63]. G. Zeng et al fabricated nanocomposite membranes by blending different contents of titanium dioxide-halloysite nanotubes (TiO_2-HNTs) with PVDF matrix. The contact angle (CA) tests indicated that the hydrophilicity of membranes was significantly increased with the addition of TiO_2- HNTs. The pure water flux of 3%TiO_2-HNTs/ PVDF was increased by 264.8% and 35.6%, respectively, compared with pristine

PVDF membrane and 3% TiO_2/ PVDF membrane. An excellent anti-fouling performance exhibited by TiO_2-HNTs/ PVDF membrane was attributed to hydrophilic nanoparticles which resisted the hydrophobic contaminants in waste water [64]. Safarpour M et al. [43] reported rGO/ TiO_2 blended PVDF membrane prepared by the phase inversion method. The hydrophilicity and permeability of the blended membranes were enhanced due to the addition of the rGO/ TiO_2 nanocomposite containing various oxygenated hydrophilic groups. Also, the rGO/ TiO_2 blended PVDF membranes had higher flux recovery ratios compared with the bare PVDF membrane. On the basis of the achieved hydrophilicity, pure water flux, and antifouling results, the best content of rGO/ TiO_2 nanocomposite was 0.05 wt % in the casting solution. Hence, rGO/ TiO_2 nanocomposite is an excellent antifouling additive having promising applications in the membrane field [43]. In another study it is demonstrated that PVDF/TiO_2 nanocomposite membranes displayed outstanding permeability performance tests even higher than commercially available PVDF membrane due to the extraordinary pore connectivity between the filler material and matrix [60]. Incorporation of TiO_2 also enhanced the protein resistance of membranes significantly due to hydrophilic nature of the NPs [60]. Nanocomposite membranes based on PVDF/ TiO_2 have been reported by different researchers for the degradation of dyes owing to photocatalytic effect of TiO_2 NPs. N.A.M. Nor et al., recently reported nanocomposite membrane of PVDF/TiO_2 for decomposition of organic pollutant from waste water [45]. H.P. Ngang et al developed PVDF–TiO_2 mixed-matrix ultrafiltration membrane for the degradation of methylene blue (MB). Although, the performance of the nancomposite membrane was little affected at higher concentration of MB yet it exceeded the neat PVDF membrane due to the extra adsorption sites provided by TiO_2 NPs for MB dye [37].

Energy

Much attention is paid to develop solid state lithium ions battery in order to overcome the issues like leakage of solution electrolyte, longer life cycle, high energy state density, electrochemical stability and mechanical strength [63]. Highly electronegative fluorine in the backbone of PVDF and its high dielectric constant make it a perfect choice as polymer matrix to be used as solid polymer electrolyte (SPE).Y-J. Wang et al reported SPE based on PVDF/ $LiClO_4$/ TiO_2 with enhanced conductivity upon inclusion of up to 10 wt% addition of TiO_2 nanoparticles [34].

Another group reported lithium bis (oxalato) borate (LiBOB) based PVDF/PVC composite polymer electrolyte (CPE) membrane with 2.5 wt% TiO_2 exhibiting comparatively high ambient-temperature conductivity than ZrO_2 with even porous network to accommodate liquid electrolyte. Mobility of Li^+ ions could be facilitated due to the amorphicity of the highly conductive CPE having potential to be useful as lithium-ion electrolyte batteries [64]. Similarly, electrolyte membrane based on PEO/PVDF/TiO_2 was fabricated by H. Han et al. They applied it for solid state dye-sensitized nanocrystalline solar cells. Introduction of TiO_2 and electronegative fluorine of PVDF resulted in outstanding performance of the solar cell due to high conductivity and reduced recombination rate at the interface of solid state electrolyte and TiO_2 NPs [65].

Electronics

Development of high energy density polymer-based dielectric materials has become a challenging topic of research interest [63]. Polymer matrices containing homogeneous Dispersion of metal oxide nanoparticles are of particular attention because of their potentially high breakdown strength and high dielectric permittivity. Such combinations may be used as an alternative approach to develop dielectric materials for energy storage and sensing applications. K. Prabakaran et al., reported PVDF/ HFP/ TiO_2 nanocomposite with two fold enhancement in dielectric constant upon incorporation of TiO_2 NPs [51]. In another study conducted by J. Iwagoshi et al., it is demonstrated that incorporation of rutile TiO_2 NPs into PVDF host shown promising results for their use as capacitor due to enhancement in electrical properties of the nanocomposite [66]. W. L. Ong et al focused on the development of a hybrid organic–inorganic TiO_2 nanocomposite, which were used as the volatile organic compound (VOC) sensing and photocatalytic degradation with production of hydrogen gas. These properties were enhanced by the well-structured TiO_2 nanotubes, metal nanoparticles and reduced graphene oxide loading for enhanced light absorption and charge-transfer kinetics. Crosslinking networks were induced due to functionalization of TiO_2 nanocomposite with a polyvinylidene fluoride (PVDF) matrix which produced the mechanical reinforcement-flexibility [67]. Anjum Qureshi et al investigated ac/dc electrical properties of (lithium and titanium doped nickel oxide) LTNO/ PVDF nanocomposites film as a function of temperature and as NH_3 gas sensor. It was observed that electrical conductivity obeys the power law. Spin coating method was used to fabricate LTNO/ PVDF nanocomposite which was used for the sensing of ammonia gas [68].

Meng-Fang Lin et al reported PVDF-*g*-HEMA [poly (vinylidene fluoride)-*graft*-poly (2- hydroxyethylmethacrylate)/Barium Titanate ($BaTiO_3$) nanocomposites for high energy density capacitor materials. Highest dielectric constant up to 333 was achieved [69].

Haixiong Tanget at fabricated barium titanate ($BaTiO_3$) nanowires (NWs) in a poly (vinylidene fluoride-trifluoro ethylene-chloro fluoro ethylene) (PVDF-TrFE-CFE)) matrix. High breakdown strength and high dielectric permittivity were reported for these nanocomposites [70]. Lyly Nyl Ismail et al reported the dielectric properties of multilayer PVDF-TrFE/ PMMA:TiO_2 thin film. Spin coating method was used to fabricate these films .Due to the high dielectric properties, of these films are found to have wide applications in electronics industry [71].

Conclusion

In this mini review article we have discussed the morphology of TiO_2 nanostructures. It is shown that 1-D TiO_2 nanostructures have high aspect ratio having quite high efficiency in certain applications as for instance photocatalytic activity of TNTs is found to be 10 folds that of TNPs [23]. Apart from this, nanocomposites based on PVDF and TiO_2 demonstrate versatile applications especially in the field of environmental remediation, dielectric materials and solid state polymer electrolytes. There is still room to further explore the effect of TiO_2 doped with different metals, metal oxides and carbon nanomaterials to be used as filler materials for PVDF matrix. Also, little information is available in literature on the nanocomposites of TNTs with PVDF. TNTs can be more effective than TiO_2 nanoparticles due to the ordered structure and hence can open gate for exciting application.

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