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$_2$O$_3$ 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 (TiO2 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 TiO2 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.

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 TiO2- NPs vs Nanotubes**

Critical properties of TiO2 which should be considered for its specific application include geometry, morphology and microstructure. These properties are summarized in Table 1.

| Structure | Properties | TNPs | TNTs |
|-----------|------------|------|------|
| TNPs | TiO2 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]. | | TTNs exist as anatase phase atm/ below 450°C Where as above this temperature converts to rutile phase. However, TNTs deform at elevated temperatures [20]. |
| Morphology | TNPs are spherical in nature having zero dimension as shown below. | | TNTs are tubular in shape having one dimensional morphology. |

![Figure 1. Pictorial representation of different dimensions of NPs.](image)

Nanocomposite of PVDF with TiO2 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 an alternative 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]. TiO2 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/TiO2 nanocomposite for potential applications in variety of fields [29-30].

![Figure 2. SEM image of TNPs](image)

![Figure 3. SEM image of TNTs](image)
There is considerable impact of addition TiO2 on the formation of compact macro void in the nanocomposite matrix. The authors attributed this improvement to the methods of preparation. Moreover, enhancement in the dielectric constant of nanocomposite by K. Prabakaran et al [51]. They reported about two fold thermal and electrical properties of PVDF/ HfP as reported combination of 1 wt % Al2O3 and 2 wt % TiO2 in PVDF MPa to 3.74 MPa was observed upon incorporation of a tensile strength of PVDF hollow fibre membranes from 1.71 or method sol-gel [49]. Similarly, an improvement in the tensile strength of PVDF/TiO2 hollow fibre membranes prepared via blending and immobilized laccase by chemical coupling on membrane surface [56-63]. G. Zeng et al fabricated nanocomposite membranes, removal of heavy metals and photocatalytic degradation of dyes in textile industry [55]. TiO2 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 (TiO2-HNTs) with PVDF matrix. The authors attributed this improvement to the formation of compact macro void in the nanocomposite [50]. There is considerable impact of addition TiO2 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 TiO2 NPs. Moreover, significant changes in optical properties of PVDF could be observed by incorporation of TiO2.

L.Yu et al., reported 30% enhancement in tensile strength of PVDF/TiO2 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 % Al2O3 and 2 wt % TiO2 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 TiO2 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 TiO2 NPs. Moreover, significant changes in optical properties of PVDF could be observed by incorporation of TiO2.

NPs e.g., Zhang et al and A. Munoz-Bonilla et al have reported the transmittance spectra of PVDF/ ZrO2-TiO2 and PVDF/TiO2 nanocomposite [52-53]. They showed an increase in the absorption and refractive index of the nanocomposite in the presence of TiO2 NPs. In fact, enhancement in different properties of PVDF/TiO2 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 Ti4+ ions via Vander Waal forces of interaction to induce mechanical stability to nanocomposites for various exciting applications as shown pictorially in figure 4 [54].

The cumulative effect of both PVDF and TiO2 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/ TiO2 nanocomposites are briefly reviewed (fig 5).

**Table 2. Nanocomposites based on PVDF/TiO2**

| Nanocomposites | Content of TiO2 | Methods of preparation | Uses | References |
|----------------|----------------|------------------------|------|------------|
| PVDF-HFP/TiO2  | <50%           | Phase inversion and conventional casting methods | Polymer electrolytes in fuel cells | 31 |
| PVDF-HFP/TiO2  | 40% rulite     | fuel cells              |      | 32 |
| PVDF-HFP/TiO2  | 15%            | Phase inversion method  | fuel cells electrolytes in fuel cells | 33 |
| PVDF/HFP/TiO2  | 10%            | In situ sol-gel process | Polymer electrolytes in lithium ion batteries | 34 |
| PVDF/HFP/TiO2  | 6.5%           | Phase inversion method  | fuel cells electrolytes in fuel cells | 35 |
| LiDFOB-based PVDF-HFP/TiO2 | 5% | Solid state reaction method | Polymer electrolytes in fuel cells | 36 |
| PVDF/HFP/1%OA | 1%             | Sol gel                 | Degeradation of methyl orange | 38 |
| PVDF/HFP/2%OA | 0-4%           | Casting solution        | Degeradation of Reactive Black 5 | 39 |
| PVDF/HFP/1%OA | 0.5%           | Phase inversion technique| Degeradation of Brilliant Green, Indigo Carmine | 40 |
| Poly (vinylidine fluoride) plasma- grafted poly(acrylic acid) membrane/TiO2 | 0.5% | Casting solution | Degeradation of Reactive Black 5 | 41 |
| PVDF/1%TiO2   | 0.5%           | sol-gel process and immobilized laccase by chemical coupling on membrane surface | Removal of BPA as high as 90 % | 42 |
| PVDF/1%GO     | 0.05%          | phase inversion method  | Show best fouling resistance | 43 |
| PVDF/1%GO     | 1-2wt.%        | melt-intercalation method | Increase mechanical and tribological properties of membrane | 44 |
| PVDF/1%GO     | 0.5%           | low temperature hydrothermal (LTH) process | membrane distillation | 45 |
| PVDF/1%GO     | 0.7wt%         | Amorphous phase separation | Improved the hydrophilicity | 46 |
| PVDF/1%GO     | 0-4%           | phase inversion induced by dry-jet spinning method | best adsorption capacity of lead | 47 |
| PVDF/1%GO     | 2wt.%          | removal of oil          |      | 48 |

**Environmental application**

Extensive reports are available in literature for the utilization of PVDF/ TiO2 nanocomposite as water treatment membranes, removal of heavy metals and photocatalytic degradation of dyes in textile industry [55]. TiO2 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 (TiO2-HNTs) with PVDF matrix. The contact angle (CA) tests indicated that the hydrophilicity of membranes was significantly increased with the addition of TiO2- HNTs. The pure water flux of 3%TiO2-HNTs/ PVDF was increased by 264.8% and 35.6%, respectively, compared with pristine
PVDF membrane and 3% TiO2/ PVDF membrane. An excellent anti-fouling performance exhibited by TiO2-HNTs/ PVDF membrane was attributed to hydrophilic nanoparticles which resisted the hydrophobic contaminants in waste water [64]. Safarpour M et al. [43] reported rGO/ TiO2 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/ TiO2 nanocomposite containing various oxygenated hydrophilic groups. Also, the rGO/ TiO2 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 anti-fouling results, the best content of rGO/ TiO2 nanocomposite was 0.05 wt% in the casting solution. Hence, rGO/ TiO2 nanocomposite is an excellent anti-fouling additive having promising applications in the membrane field [43]. In another study it is demonstrated that PVDF/TiO2 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 TiO2 also enhanced the protein resistance of membranes significantly due to hydrophilic nature of the NPs [60]. Nanocomposite membranes based on PVDF/ TiO2 have been reported by different researchers for the degradation of dyes owing to photocatalytic effect of TiO2 NPs. N.A.M. Nor et al., recently reported nanocomposite membrane of PVDF/TiO2 for decomposition of organic pollutant from waste water [45]. H.P. Ngang et al developed PVDF–TiO2 mixed-matrix ultrafiltration membrane for the degradation of methylene blue (MB). Although, the performance of the nanocomposite membrane was little affected at higher concentration of MB yet it exceeded the neat PVDF membrane due to the extra adsorption sites provided by TiO2 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/ LiClO4/ TiO2 with enhanced conductivity upon inclusion of up to 10 wt% addition of TiO2 nanoparticles [34].

Another group reported lithium bis (oxalato) borate (LiBOB) based PVDF/PVC composite polymer electrolyte (CPE) membrane with 2.5 wt% TiO2 exhibiting comparatively high ambient-temperature conductivity than ZrO2 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/TiO2 was fabricated by H. Han et al. They applied it for solid state dye-sensitized nanocrystalline solar cells. Introduction of TiO2 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 TiO2 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/ TiO2 nanocomposite with two fold enhancement in dielectric constant upon incorporation of TiO2 NPs [51]. In another study conducted by J. Iwagoshi et al., it is demonstrated that incorporation of rutile TiO2 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 TiO2 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 TiO2 nanotubes, metal nanoparticles and reduced graphene oxide loading for enhanced light absorption and charge-transfer kinetics. Crosslinking networks were induced due to functionalization of TiO2 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 NH3 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 (BaTiO3) nanocomposites for high energy density capacitor materials. Highest dielectric constant up to 333 was achieved [69].

Haixiong Tanget at fabricated barium titanate (BaTiO3) 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/TiO2 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 TiO₂ nanostructures. It is shown that 1-D TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ nanoparticles due to the ordered structure and hence can open gate for exciting application.

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