Comparative **study of Synthesis of PVA, PVA/TiO_2, PVA/ZrO_2 and PVA/ TiO_2/ZrO_2 composite membranes**

[1] Dr Jyotsna Chauhan,[2]akansha mehto, [3]Shaswat Chauhan

[1]Professor in RGPV,[2]Research scholar ,[3] BITS Pilani GOA

Abstract: This paper explores polymeric nanocomposites based on refractory ceramic oxides with special emphasis on polyvinyl alcohol (PVA) as the host matrix. The aim of the study is to synthesizing TiO_2, ZrO_2 nanoparticles and their nanocomposite membranes for improving the structural, optical and morphological characteristics of nanocomposite membrane.. The use of PVA as a host matrix is justified by highlighting its remarkable properties, including mechanical strength, flexibility, and film-forming ability. A thorough explanation of PVA's hydrophilic properties and its wide range of uses from food packaging to sensors, supercapacitors, catalysts, and more is then discussed.

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Introduction:

It has been noted that the optical properties of nanocomposites have improved with the addition of both organic and inorganic constituents. These nanocomposites therefore have potential applications in a variety of fields, such as gas sensors, solar cells, super capacitors, and flexible electronics. The present study investigated the doping effects of different phases of TiO_2 upon the PVA membranes structural, morphological, optical and photoluminescence characteristics. TiO_2 nanoparticles prepared by sol-gel technique and different phases successfully achieved by controlling calcination temperature. PVA/TiO_2 membranes were then fabricated by solution casting method.. Sol-gel method was used for producing TiO_2 and ZrO_2 nanoparticles, while solution casting approach was used to prepare PVA and PVA/nanoparticles composite membranes. The solution casting technique is the simplest and most effective technique to get the best possible dispersion of nanoparticles within nanocomposites. The diverse uses of polymer nanocomposites in packaging of food, coatings, air and water purification, batteries and solar cells have led to substantial research into these materials [1-4]. Among the different polymer polyvinyl alcohol (PVA) focused much attention as result of its distinctive qualities, like environment friendly, solubility in water, non-toxic, biodegradable, excellent optical and electrical properties, charge storage capability and chemical stability [5-8]. Several studies show the different applications of PVA when tuned its optical and structural properties by doping [9-13]. The OH group in PVA is responsible for majority of the physical properties that gives rise to the substances wide range of industrial uses [14].

Nanocomposites made of an organic polymer and inorganic material are gaining a much attention because of their outstanding properties and numerous uses [15-17]. The fabrication of inorganic and organic hybrid systems devices like optoelectronic devices, solar cell and photoelectrode can result in the invention of novel devices technologies [18-20]. Polymer/ceramic oxide composites have also received a lot of research attention for the separator of supercapacitors [21, 22]. Lithium-ion batteries are promising alternatives for portable gadgets and electric cars because of its small size, cheap maintenance, extended life cycle and higher energy density [23]. However, increasing the lithium-ion batteries use into novel energy storage devices with low self-discharge requires improved battery safety [24-26]. Yanilmaz et al. reported separators play a crucial role to prevent short circuits through restricting physical connection between electrodes. Simultaneously, allowing the movement of lithium-ions between them during cycles of charging and discharging. The separators must have appropriate pore size, exceptional thermal and chemical stability, sufficient thickness and superior permeability to lithium-ions. [27].

Xiao et al. reported that PVA serves a famous as a superior material for membranes because of its exceptional qualities including good film-forming ability and superior mechanical, chemical, and thermal stabilities. Numerous investigations have been conducted since the introduction of membranes based on PVA as separators in diverse fuel cells. PVA, a crucial component of the gel electrolyte in microbial fuel batteries, has generated a lot of interest [28]. Doping of inorganic ceramic oxide

nanoparticles can enhance characteristics of PVA membranes. It has been discovered that doping of ceramics oxides to the polymer matrix increases ionic conductivity because they add porosity to the PVA matrix by expanding the amorphous areas of the crystalline polymer [29]. According to studies, incorporating inorganic particles into separator membranes is a good strategy to increase thermal stability and electrochemical performance [30-33].

A lot of interest has been paid to titanium dioxide (TiO_2) because of its promising qualities. It is an inorganic semiconductor with a large band gap that finds extensive use in various fields, such as air and water purification, photocatalysis, sensors and self-cleaning windows [34]. Anatase, brookite and rutile is the three main phases of TiO_2. The utmost stable phase of TiO_2 was discovered to be rutile, while the other two (anatase and brookite) are metastable forms [35, 36]. When TiO_2 and PVA polymer are combined, they may interact in the polymers crystalline or amorphous regions, changing its electrical, structural and optical characteristics [37].

Gupta et al. reported the ball milling process for the preparation of TiO_2 nanoparticles in order to increase the photocatalytic activity and mechanical strength and suggest that by optimizing the rotating speed, ball to grinding material ratio and grinding time the desired properties of grinding material may be tuned [38]. Ramakrishnan et al. investigated solvothermal and microwave techniques to produce TiO_2 nanoparticles for use in dye-sensitized solar cells

Experimental:

1.1.1. Sol-gel synthesis of TiO_2 nanoparticles:

We used the sol gel method to synthesize TiO_2 nanoparticles. The synthesis procedure flow chart is given in Figure 3.1. For TiO_2 nanoparticles first we have prepared the solution of ethanol and methanol then we add TTIP in the solution while stirring continuously. The mixtures pH were maintained at 2 to 3 through the addition of drop of HCl and we have put the solution on magnetic stirrer for 2 to 3 hours. After that the reaction is stop by adding water and again stirring on magnetic stirrer for 1 to 2 hours. After Ageing at room temperature for three days the sample was dry at 85 °C, at hot plate and then grinding for 30 minutes. For obtain different phases of TiO_2 the sample was calcinated at 300 °C, 600 °C and 1000 °C for brookite, brookite -rutile and rutile phase respectively.

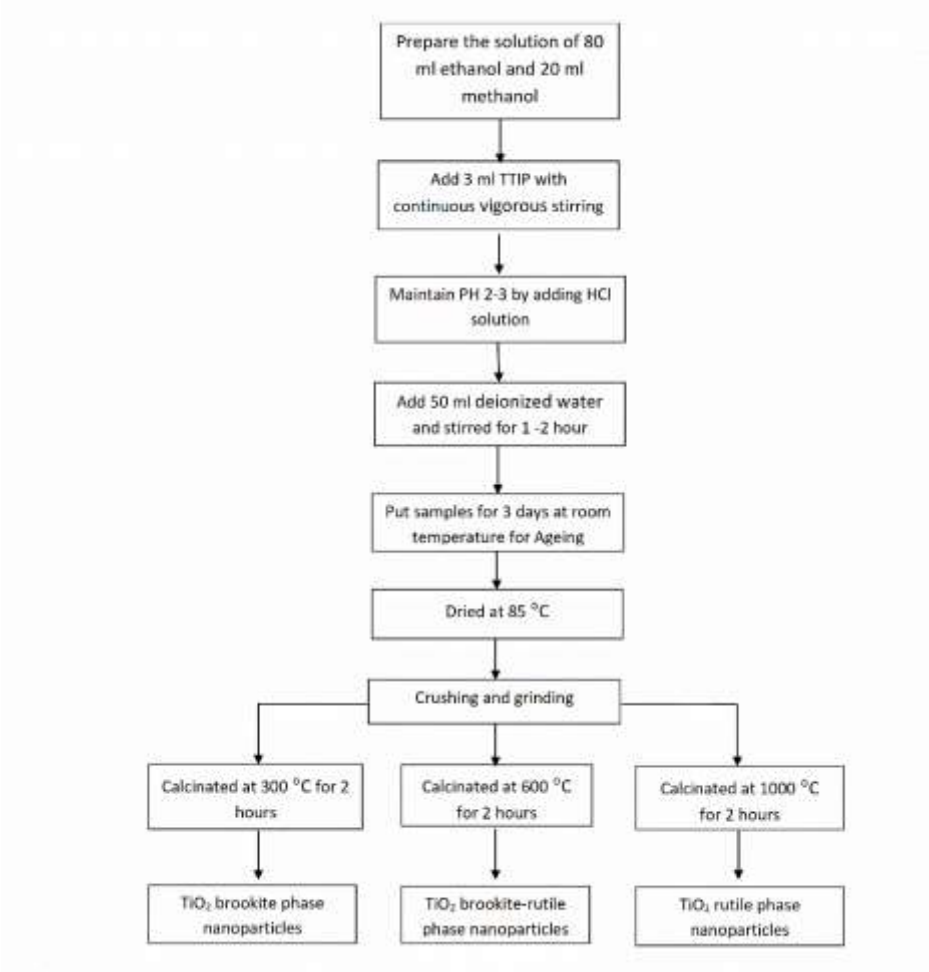

Figure. 3.1: TiO_2 nanoparticles synthesis flow chart.

1.1.2. PVA and PVA/TiO_2 membranes preparation:

Composite membrane of PVA/TiO_2 has been prepared using solution casting process. To obtain pure and homogeneous PVA solution, the process involved, 1 gram of PVA was dissolved in 20 ml of distilled water, then at 80 °C the mixture was continuously stirred until complete transparency was achieved. In another beaker, TiO_2 (0.05 gram) were mixed in distilled water (10 ml), subsequently, sonicated for 1 h. In order to prepare TiO_2 doped PVA membranes, the two solutions were combined and sonicated the mixture for a duration of 2 hours to achieve TiO_2 nanoparticles uniform dispersion in PVA. The resultant mixture was transferred to a Petri dish then left two days for drying at ambient temperatures. After completely dried, the films were removed out of the Petri dish. The same procedure also repeated to prepare PVA/TiO_2 membrane with different phases of TiO_2 (brookite, brookite-rutile and rutile).

4.1.1. ZrO_2 nanoparticles Synthesis:

We synthesized ZrO_2 nanoparticles using the sol-gel method. For obtaining ZrO_2 nanoparticles zirconium acetate hydroxide (0.058M) was dissolved in deionized water (100 ml) under constant stirring on magnetic stirrer for 30 minutes and then maintaining a pH of 7-8 by slowly adding of NH_4OH solution.

To enhance aging, the reaction mixture was kept at room temperature overnight under continuous constant stirring and after that centrifuged to remove water. The sample were washed with water and ethanol and filtered with filter paper. The recovered gel was dried at 70°C then crushed to get fine powder and calcined at 650 °C for 2 hours to obtain ZrO_2 nanoparticles.

We used solution casting technique for the preparation of PVA and PVA/ZrO_2 nanocomposite membranes with various loading of ZrO_2 nanoparticles (5 wt%, 9 wt% and 13 wt%). A pure and homogeneous solution of PVA was obtained by dissolving 1 gm of PVA into 20 ml deionized water and stirring vigorously at 80°C until transparent solution. At the same time ZrO_2 nanoparticles (5 wt%) were dispersed in 10 ml of deionized water separately by sonication at ambient temperature for 3 hours and then added with PVA solution. The solution was again stirred for 1 hour with the magnetic stirrer and sonicated for 30 minutes. The resulting PVA-ZrO_2 solution was poured on clean, dried Petri dish and left to dry for two days at room temperature. The dried PVA/ZrO_2 (5 wt%) composite membrane was peeled off from the Petri dish and cut into required size for further analysis. Same process was also repeated for the preparation of PVA/ZrO_2 (9 wt%) and PVA/ZrO_2 (13 wt%) composite membrane.

Preparation of PVA/ZrO_2 composite membranes:

We prepared PVA/ZrO_2 nanocomposite membranes with various loading of ZrO_2 nanoparticles (5 wt%, 9 wt% and 13 wt%). A pure and homogenous PVA solution was prepared by dissolving 1 gm of PVA in 20 ml distilled water and stirred at 80°C until a transparent solution was obtained. Simultaneously, ZrO_2 nanoparticles (5 wt%) were separately dispersed in 10 ml of deionized water through sonication at room temperature for 3 hours and then combined with PVA solution. The mixture of PVA and ZrO_2 was stirred for 1 hour and sonicated for 30 minutes. The resulting solution was poured in petri dish and dry at room temperature for two days. The dried composite membrane was peeled off from the Petri dish. We also prepared PVA/ZrO_2 (9 wt%) and PVA/ZrO_2 (13 wt%) composite membranes by repeating same procedure.

2.1.1.1. Preparation of PVA/TiO_2/ZrO_2 composite membranes:

PVA/TiO_2/ZrO_2 composite membranes were synthesized using a simple solution casting technique. To prepare the PVA solution, a known amount (1 g) of PVA was dissolved in 20 ml distilled water and stirred at 80°C until the solution turned transparent. At the same time, to prepare TiO_2 and ZrO_2 solution 0.05 g of each TiO_2 and ZrO_2 nanoparticles were dispersed in 10 ml distilled water in separate beakers by ultra sonication. Then the prepared TiO_2 and ZrO_2 solution were directly mixed with the PVA solution. The mixture was stirred and sonicated for 1 hours to achieve homogeneous dispersion of TiO_2 and ZrO_2
nanoparticles in the PVA and the resulting solution was poured in Petri dish. After drying, obtained uniform ceramic oxides dispersed PVA membranes were removed from the Petri dish.

Polyvinyl alcohol (PVA) with a purity of 4 N (molecular weight = 85,000 to 124,000) purchased from Central Drug House (P) Ltd. Titanium tetraisopropoxide (TTIP) used as TiO_2 precursor obtained from Avra Synthesis Pvt. Ltd. Hydrochloric acid (HCl) and distilled water also purchased from Central Drug House (P) Ltd.

4.2. Results and Discussion:

In pure zirconia, there are three different crystal structures: monoclinic, m- ZrO_2, tetragonal, t- ZrO_2, and cubic, c- ZrO_2.The structure is defined by a unit cell, which is a repeating unit that forms the crystal lattice. Figure 4.1 illustrates the crystal structures of tetragonal ZrO_2. In the tetragonal phase, this unit cell has a rectangular shape, and its dimensions are typically described by two lattice parameters, often denoted as "a" and "c." Zirconium atoms are located at the corners of the rectangular unit cell and form a square lattice along the shorter "a" axis. These Zr atoms are positioned at the vertices of the unit cell.

Oxygen atoms are positioned between the zirconium atoms along the longer "c" axis. In this arrangement, oxygen atoms form layers that separate the layers of zirconium atoms. The oxygen atoms are closely packed in a way that maximizes their interactions with the zirconium atoms. Tetragonal ZrO_2

exhibits
good ionic conductivity, high strength, and fracture toughness [17]. Tetragonal zirconia (t-zirconia) exhibits greater toughness compared to monoclinic (m-) and cubic (c-) ZrO_2, as well as other ceramic materials. Therefore, it serves as a toughening agent for other ceramic materials. These materials are referred to as zirconia toughened ceramics. This structure is closely related to the cubic ZrO_2 structure but differs in two respects, Firstly, In the lattice, there is a distortion, corresponding to a slight c-axis elongation. Secondly, oxygen atom columns are displaced alternately up or down the c axis. As a result, four oxygen neighbours are moved closer to a zirconium atom and the four other oxygen neighbours move away from it. The presence of these interdependent distortions are necessary to prevents O–O contact [18]. Each atom of zirconium maintains its eight-fold coordination with oxygen. It consists of four oxygen atoms at a distance of 2.1 Å atoms, and another four at a distance of 2.3 Å atoms.

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