A Review of HCL-Doped- Polyaniline, Tio2 Nanoparticles and P-Toluene Sulfonic Acid Doped Polyaniline:Titanium Dioxide Nanocomposite

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Abstract – The initial results on polymer reinforcement of nanoparticles are incompatible with the improvements in the resulting nanocomposites ' fundamental thermal and mechanical properties. It soon became apparent that a multitude of parameters affected the overall performance of nanocomposites such as the dispersion and distribution of nanoparticles, the transfer of load from nanoparticles to matrix, the geometric arrangement of nanoparticles, the nano-scale mechanical reaction of nanoparticles, the formation and properties of interphase polymers as well as the chemical modification of nanoparticles. Originally, the most important factor was the dispersion of nanoparticles, where increasing the clustering of nanoparticles contributed to better dispersion and improved the contact area between polymer and nanoparticles. With improved processing methods leading to better distributed systems, the rise in nanocomposite modules is now more clear, but there is still more or less elusive growth in strength and durability.

Keywords: Hcl-doped- polyaniline, tio2 nanoparticles, p-toluene sulfonic acid doped polyaniline:titanium dioxide and nanocomposite.

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I. INTRODUCTION

Nanocomposite materials are those that combine two or more individual components to improve quality properties where at least one dimension of a component's distributed particles is within the range of nanometers. The application of high-modulus filler, for example, increases a polymer's modulus and power. Unfortunately, this often occurs in conventional composites at the expense of a significant reduction in ductility and sometimes in impact strength due to concentrations of stress caused by the fillers. On the other hand, well-dispersed nanoparticles can enhance the module and strength and retain or even increase ductility as their small size does not create large concentrations of pressure. Numerical simulations estimate tensile modules in the range of 1 TPa for CNTs making them the ultimate filler material with high stiffness. [1]

II. CLASSIFICATION OF NANOCOMPOSITES

Depending on the nature of the distributed phase and dispersion medium, nanocomposites can be divided into the following four groups. Inorganic-organic nanocomposites: for example, nanoclusters / particles of metal or semiconductor distributed in a polymer matrix (such as polymethyl methacrylate and block copolymers). Organic-inorganic nanocomposites: for example, organic dyes or biopolymers nanoparticles dispersed in an inorganic matrix (such as silica, titanium or alumina). Inorganic-inorganic nanocomposites: for example, silica matrix disperses gold nanoparticles. Organic-organic nanocomposites, such as organic dyes nanoparticles dispersed in the polymethylmethacrylate matrix. [2]

III. POLYMER NANOCOMPOSITES

Polymer nanocomposites are the polymer matrices which include randomly distributed nanoparticles and/or clusters of nanoparticles within the polymer matrices. The nanoparticles in such composites therefore serve as the dispersed phase, while the polymer matrix serves as the medium of dispersion. Nanoparticles can be viewed as microencapsulated particles in the shells of polymers. Recently, there have been studies of nanocomposites whose nanoparticles were found only on the surface of the polymer particles, fibers, films. Also used are nanocomposites containing 3D, 2D and 1D structures of nanoparticles. [3]

IV. PROPERTIES OF NANOCOMPOSITES

The increase in desirable properties and the emergence of new properties in the materials using nanoscale reinforcement inspired the explosive analysis of the properties of nanocomposites and their applications are as follows: the primary reason for adding inorganic filler particles to polymer matrices is to boost their mechanical efficiency. In addition, numerical simulations and experimental findings suggest large elastic (recoverable) nanotubes strains. Other forms of nanoreinforcements like nanoclays and graphite nanoplatelets also have high modulus values for nanocomposites, i.e. high enhancement of stiffness. [4]

- **Strength- and stiffness-to-weight ratios**: Because of the exceptional mechanical properties and low densities associated with typical nanoreinforcements, nanocomposites with high volume fractions of nanoinclusions can result in weight resistance and rigidity ratios that cannot be achieved with conventional composite materials. To weight-critical applications, it offers significant weight savings. Hybrid multiscale composites were also proposed in traditional micro-sized fibrous composites where nanoreinforcement is added to the matrix material. [5]

- **Multifunctionality**: Nanotubes and other forms of nano-reinforcement were also shown to have exceptional electrical and heat-related properties in addition to their outstanding mechanical properties. It means that, in addition to some other secondary material properties, the structures can be designed to meet mechanical requirements. For example, nano-reinforcement fractions of low volume (weight) were used to enhance electrical conductivity, increase working temperature, and improve the barrier and diffusion properties of polymers (primarily for platelet-shaped reinforcement) in addition to improving mechanical properties. [6]

- **Electrical and Optical Properties**: Polymer nanocomposites ' electrical and optical properties are exciting research fields. This becomes particularly important due to the possibility of making composites with different combinations of functionalities such as electrically conducting composites with better optically transparent wear resistance. These properties can result because when embedded in transparent matrices, the nanoparticles show their physical solid-state properties. Optical composites are classified as composites that consist of optically active nanoparticles that are often a polymer embedded in a transparent host material. [7]

Optical composites take advantage of the optical properties of materials that are difficult to grow in the form of single crystals or need environmental protection and provide them with the ease of processing that many polymers have. However, for certain specific applications, nanoscale particles are required to achieve specific optical properties in materials, while the function of the polymer matrix is simply to keep the particles together and provide processability. For example, the use of polymer molding techniques made accessible high-grade optical composites with properties previously obtainable only in optical glasses. [8]

V. PREPARATION OF NANOCOMPOSITES

Through polymer matrix, there are several ways to distribute nanoparticles. Few of them will be discussed below.

Direct/melt mixing

Direct mixing benefits from well-established techniques for polymer processing. This method involves the mechanical mixing with polymer matrix of organically altered inorganic nanoparticles. For example, in a two-roll mill, polypropylene and nanoscale silica were successfully mixed, but the samples were more than 20 wt. It was impossible to draw a proportion of the filler. Melt mixing is the best way to introduce new nanocomposites to the world market as it can take full advantage of well-constructed polymer processing equipment like extruders and injectors. [9]

Solution mixing

This is a very simple method which involves nanoparticles being dispersed in a polymer solution followed by solvent drying. This method is relatively easy and this method can be used to prepare nanocomposites by commercially available nanoparticles. The idea of combining solutions to create nanocomposites. Nevertheless, in order to spread the nanoparticles homogenously in the polymer matrix, this method requires thorough mixing. Great care must be taken to prevent flocculation or agglomeration that can sometimes result in inhomogeneous distribution of nanoparticles within the matrix of polymers.

To order to make it compatible with the polymer matrix, greater dispersibility could be accomplished by pretreating the surface of nanoparticles. This procedure leads to ease of movement within the polymer matrix of the nanoparticles. If a crucial condition is not the homogeneity of nanoparticles dispersion, this preparation approach is very promising. However, if the homogeneity of the nanocomposite is a vital condition, the approach is not so promising. In optical applications, the problem with such inhomogeneous nanocomposites may include the disadvantageous scattering which results in reduced material quality. [10]

VI. APPLICATIONS OF NANOCOMPOSITES

- **Polymer nanocomposite has emerged as a promising organic-inorganic material class. Different chemistries between constituents can lead to various nanocomposite applications.**

- **Producing batteries with greater power output:** Researchers have developed a method for making anodes from a composite formed with silicon nanospheres and carbon nanoparticles for lithium ion batteries. The silicon carbon nanocomposite anodes make closer contact with the lithium electrolyte, allowing for faster power charging or discharge.

- **Speeding up the healing process for broken bones:** Studies have shown that replacement bone growth is accelerated by using a nanotube-polymer nanocomposite as a form of scaffold that guides replacement bone growth. To better understand how this nanocomposite improves bone growth, the studies are conducting studies.

- **Producing structural components with a high strength-to-weight ratio:** An epoxy containing carbon nanotubes, for example, can be used to produce composite windmill blades of nanotube-polymer. This results in a solid but lightweight blade that makes it practical to use longer windmill blades. Such longer blades raise each windmill's amount of electricity.

- **Using graphene to make composites with even higher strength-to-weight ratios:** Researchers have found that using a similar weight of carbon nanotubes, the addition of graphene to epoxy composites could result in stronger / stiffer components than epoxy composites. Graphene tends to bind stronger with the polymers in the epoxy, allowing the graphene to be incorporated more easily into the composite structure. This property can contribute to the manufacture of components with higher strength-to-weight ratios for applications such as windmill blades or components of aircraft.

- **Making lightweight sensors with nanocomposites:** Electricity is induced by a polymer-nanotube nanocomposite; how well it conducts depends on the nanotubes spacing. This property allows patches of nanocomposite polymer-nanotube to act on windmill blades as stress sensors. The nanocomposite will also bend if strong wind strikes the blades. Bending affects the electrical conductance of the nanocomposite detector, allowing an alarm to sound. This warning would make it possible to shut down the windmill before unnecessary damage occurs.

- **Using nanocomposites to make flexible batteries:** For making a conductive sheet, a nanocomposite of cellular materials and nanotubes could be used. A versatile battery is created when this conductive paper is immersed in an electrolyte.

- **Making tumors easier to see and remove:** Scientists are trying to incorporate magnetic nanoparticles and fluorescent nanoparticles into a magnetic and fluorescent nanocomposite layer. The nanocomposite particle's magnetic activity makes the tumor more noticeable during a pre-operative MRI treatment. The nanocomposite particle's fluorescent property can help the surgeon better see the tumor during surgery. [11]

VII. THERMAL STABILITY, ELECTRICAL CONDUCTIVITY AND AMMONIA SENSING STUDIES ON p-TOLUENE SULFONIC ACID DOPED POLYANILINE:TITANIUM DIOXIDE (pTSA/PANI:TIO_2) NANOCOMPOSITE

Due to better properties and wide range of applications, the production of organic-inorganic composite materials has increased in recent years. Due to the interesting possibilities for their structural modifications and exciting potential applications in chemistry, biology, medicine and material science, these nanocomposites have gained greater attention over the past decade. Nanocomposites with different electrical, catalytic and optical properties can be mixed with a wide range of organic and inorganic materials.

Due to its good environmental stability, fast doping or dedoping by chemical means and simple synthesis, Pani receives special attention among conducting polymers as it can be readily prepared in bulk under controlled conditions by chemical oxidative polymerization of aniline. Pani shows enough stability for practical applications compared to many other n-conjugated polymers. Through adding inorganic particles, the properties of these conductive polymers can be changed. Thanks to the interesting properties of the nanosize and large surface area, nanoscale particles are more attractive. [12]

Nanoscale fillers may be added to enhance the polymers ' electrical and sensing properties. To date, a number of different particles of metal and metal oxide have been encapsulated in the shell of conducting polymers, resulting in a host of nanocomposites. Pani: TiO2 nanocomposite has received considerable interest in recent years among the various nanocomposites of Pani with inorganic nanoparticles, Xia and Wang have prepared Pani: TiO2 nanocomposite with ultrasonic irradiation. Schnitzler and Zarbin obtained TiO2 nanoparticles and Pani hybrid materials based on the technique of sol-gel.

The addition of TiO2 nanoparticles enhances Pani's conductivity and the surfactant increases TiO2 nanoparticles ' dispersibility in macromolecules. In this study, by in-situ deposition technique, we prepared composites of^TSA / Pani and TiO2 nanoparticles. The form of dopant used has a major impact on nanocomposite properties. Compared to other approaches, the synthesis approach used here is very simple and has great potential for engineering marketing. There was also research into the composition, morphology, thermal stability and conductivity of nanocomposites. [13]

VIII. THERMAL STABILITY OF HCL-DOPED- POLYANILINE AND TIO_2 NANOPARTICLES BASED NANOCOMPOSITES

With the groundbreaking discovery of the emergence of metallic range electrical conductivity in polyacetylene after reaction with some oxidizing agent, work on electrically conductive polymers has sprung to suddenly incredible heights. Out of the large number of conductive polymers explored, Pani deserves primary importance as it possesses the best combination of properties such as low cost, excellent environmental stability, customizable and reversible electrical properties through controlled load transfer processes. This makes Pani a flexible product for use in primary and secondary batteries, microelectronics, sensors and actuators.

In contrast to several other nanoparticles, titanium dioxide (TiO2) is extremely attractive due to its excellent physical and chemical properties as well as broad potential uses in various areas such as coatings, solar cells and photocatalysis. Nanocomposites based on conducting polymers and inorganic nanoparticles have recently attracted attention as it appears to be the future route for improving material quality in devices. Many studies have already been published on the synthesis of Pani's nanocomposites with nanoparticles Fe3O4, ZnO, ZrO2, montmorillonite, Au and Ag. [14]

There are several articles on Pani: TiO2 nanocomposites in-situ synthesis. Jing Li used Pani: TiO2 nanocomposite as a photocatalyst to study the photodegradation of methyl orange under sunlight. A. Dey researched Pani: TiO2 nanocomposites ' electrical and dielectric properties and also found that nanocomposites had a lower dielectric constant than Pani or TiO2. Likewise, M. R. Karim studied the electrical properties and found that the electrical parameters are highly dependent on the nanocomposite weight percentage of TiO2 nanoparticles. Thus, most of Pani's previously reported TiO2 based nanocomposites were prepared in the form of powders.

Rarely has been reported the work on Pani: TiO2 films, which seems to be due to Pani's poor processability. Recently, it has been observed that in some selected solvents such as N-methyl2-pyrrolidone (NMP), tetra methyl urea (TMU), formic acid, etc., Pani can be plasticized, offering new possibilities for Pani processability. The variance of electrical conductivity as a measure of sensing response has been successfully exploited by several studies published on the use of conductive polymers in chemical sensors. [15]

A change in electrical property indicates whether or not the conductive polymer shows sensing response while the extent of the change in electrical conductivity indicates its resistance to the observed chemical species. The thin films of Pani and Pani: TiO2 nanocomposites have recently been reported to exhibit faster response, shorter recovery time and higher sensitivity when exposed to NH3 at room temperature.

Since electrical conductivity is an important parameter used to compare most of the properties that lead to a wide range of conductive polymers applications, it needs to be investigated. No systematic work on the stability of Pani and Pani: TiO2 films in terms of preservation of electrical conductivity during accelerated ageing experiments has been published to the best of our knowledge. Further work therefore needs to focus on the conductivity aspects of nanocomposites based on Pani.

In this study, we record preparation of Pani and Pani: TiO2 nanocomposite thin films using NMP as a solvent followed by extraction of methanol to eliminate trapped NMP. HCl doped the films and calculated the electrical parameters. Pani: TiO2 nanocomposite films exhibited different electrical behavior depending on the amount of TiO2 nanoparticles compared to Pani's. In terms of conservation of electrical conductivity, the surface morphology and thermal stability were also investigated. [16]

IX. THE COMPOSITE BASED ON NANOSTRUCTURED POLYANILINE AND MULTI-WALLED CARBON NANOTUBES

The discovery of inorganic superconductive polysulfur nitride and organic electrically conductive polyacetylene caused by leaps and bounds the research activities of electrically conductive conjugated polymers. Subsequently, many other conjugated polymeric structures such as polyphenylene, polypyrrole, polythiophene, polyaniline, etc. and their derivatives are found to possess high electrical conductivity when oxidizing or reducing agents respond.

Because of its excellent environmental stability, tailorable and reversible electrical properties through controlled charge transfer processes, Pani has been widely investigated since its discovery about three decades ago. In many applications, remarkable switching capability of these electroactive polymers between conductive (doped) and isolating (undoped) states is the basis for their use. This makes Pani a versatile material that can be used in primary and secondary batteries, microelectronics, sensors and actuators etc. as electrodes. [17]

Because of their exceptional structural, mechanical and electronic properties among the nanomaterials, CNTs are extremely attractive materials. In the formulation of conducting and insulating polymer composites, they have emerged as possible products in pristine form as well as fillers for conducting as well as insulating polymer matrices. Because of these exceptional properties of the two, Pani's composite formulations as matrix with CNT as filler are expected to show several new combinations of electrical, electronic and mechanical properties compared to their individual components. CNT-based polymer nanocomposites can find applications in polymer composites reinforced with nanotubes, nanoelectronic devices, field emitters, SPM test tips, etc. In this study, in the presence of MWCNT and cetyl-trimethylammonium bromide (CTAB), we have prepared nanocomposites by in-situ oxidative polymerization of aniline. Pani and Pani thus prepared: MWCNT nanocomposites demonstrated varied electrical response depending on the amount of MWCNT in the nanocomposites. Nanocomposites ' structure, morphology, and thermal stability were also investigated. [18]

CONCLUSION

In order to address the novel properties of polymer nanocomposites, it is important to establish and use synthetic methods that control the distribution, dispersion and interaction of particle size. Synthetic techniques for nanocomposites are quite different from those for traditional microscale-filled composites, and the physiochemical variations between each process make it impossible to establish one standard technique for the production of polymer nanocomposites. That polymeric system can involve the creation of a special set of processing conditions, and in general, specific synthetic techniques can produce none-equivalent results. Despite numerous challenges, substantial research has been done to establish suitable synthetic techniques as evident from the literature to make good polymeric nanocomposites. Therefore it can be concluded that after the first step the nanocomposites are stable semiconductors. The difference can be attributed to moisture removal, excess HCl, or aniline oligomers with low molecular weight. The continuous annealing effect of temperature cycles can be due to the further variation in the electrical activity from cycle 2 onwards. Pani anomalous behavior: TiO2-2 can be due to the absence of aniline in this test of humidity, excess HCl and low molecular weight oligomers.

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