

A review on properties and applications of nano clay, silica dioxide and titanium oxide

Rahida Wati Sharudin*, Mohd Rezza Emir Mohd Azhar, Muhammad Shafiq Mat Shayuti, Suffiyana Akbar

School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Selangor, Malaysia

*Corresponding email: rahida@uitm.edu.my

Abstract

Nanoparticles have recently been used as fillers or additives in materials for different desired applications. Due to the environmental concerns and rising of nanomaterials usages worldwide, nanoparticles have been focused in research and development. An increase in consumption is indicated by various applications of nanomaterials for both commercial and domestic applications. Nanoparticles own special physical and chemical properties which help in modifying performance of materials or final products. The characterisation of nanoparticles includes crystallographic structure, surface morphology, particles' size and functional groups. Nano clays and metal oxides of titanium and silica are selected nanoparticles to be discussed on their properties that affect the performance of materials. Along with the studies investigating the properties of the nanoparticles, an interesting concern is to discover the changes in properties of materials when nanoparticles are being added. Properties include mechanical, thermal and physiochemical are improved due to the presence of the nanoparticles in the materials' matrices, thus existing the applications for the food packaging, the lubricant oils and as the antimicrobial agent. This paper reviews the physical and chemical properties of nano clay, silica oxide and titanium oxide as well as the enhanced properties of materials when being filled with nanoparticles in specific applications.

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1.0 Introduction

Over the past few decades, nanoparticles have been used as fillers or additives in materials for desired outcomes (Uddin, 2008). Nanoparticles refer to particles with a size between 1 to 100 nanometres and nanomaterials are materials with at least one component having a nanoscale size. An introduction of nanoparticles has attracted notable research and development due to their unique properties in modifying the performance of materials or final products. Various properties such as surface area, size, reactivity and others can be studied thoroughly. Worldwide consumption of nanoparticles has been constantly increased as nanoparticles deliver an improved result in qualitative characteristic of materials and create broader potentials in industries such as manufacturing industry and technology.

Nanoparticles are widely used for biomedical, environmental and other applications. As mentioned earlier, nanoparticles possess physical and chemical properties resulting changes in materials' performance. Nanocomposite's material differs from conventional composite material in terms of thermal stability, strength, flexibility, etc. The properties of nanoparticles have been studied using several of

standard characterisation methods like X-ray diffraction (XRD), electron microscopy by using scanning electron microscopy (SEM) and infrared spectroscopy by using Fourier-transform Infrared spectrometer (FTIR).

A conservative estimate made by Mordor Intelligence indicated that the global nanomaterials market was estimated around USD 4.1 billion by 2020, with a compound annual growth rate of 22% (Inshakova and Inshakov, 2017).

Quite the contrary, Allied Market Research has reported that the global nanomaterials market could hit more than USD 55 billion by 2022 from USD 14.7 billion in 2015, with a CAGR of 20.7% (Uddin, 2008). Another statistic from the European nanomaterials market, more than USD 2.5 billion of revenue generated in 2015 and is expected to reach USD 9.1 billion by 2020 with a compound annual growth rate (CAGR) of 20%.

An upward trend in global nanomaterials market value proves an increased development of nanomaterials for various applications. Contributing factors on the trend of global nanomaterials market include improvement of materials' performance, reduction in the prices of nanomaterials, increment in market penetration of existing materials, expanding

research and development of nanomaterials, generating publicity and ads, development of new nanomaterials and applications, increasing industries collaboration in which growth of international research and cooperation in production in nanotechnology industry (Inshakova and Inshakov, 2017).

Nano clays, silica oxide and titanium oxide are acknowledged for their thermal barrier property, mechanical property and toxicological property respectively, building up the interest in extensive research for desired future applications. Plus, nanomaterials are eco-friendly as they are procured from different sources and synthetisation by using green approaches. Generally, nanomaterials refer to engineered materials with one component having nanoscale dimension. Nanomaterials provide advantages from their properties, showing by their various applications that have been recognised in recent years. Due to this, development of nanomaterials is continuing to rapidly grow and achieve more outstanding results in the future.

2.0 Properties of nanoparticles

2.1 Crystallographic structures of nanoparticles

2.1.1 Nano clays

The basic arrangement of clay minerals is described in layers consisting two types of structural sheets namely octahedral (O) and tetrahedral (T), respectively. The tetrahedral part consists of oxygen and silicon linked to another tetrahedral by connecting three corners, resulting in a hexagonal structure matrix. The remaining corner is attached to the octahedral part which consists of aluminium or magnesium coordinated in six-fold with oxygen in the tetrahedral part together with hydroxyl. The two structural sheets form a layer by attraction force such as Van der Waals force, and hydrogen bonding or electrostatic force.

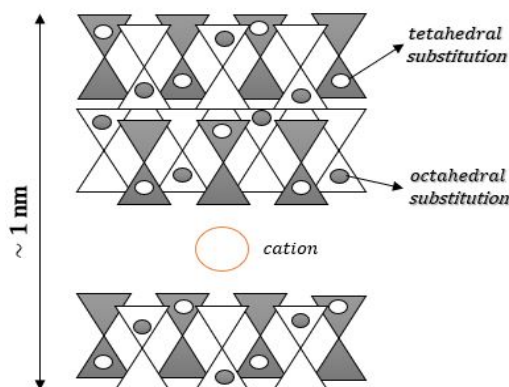


Fig. 1: Schematic structure of nano clay TOT layers and holding cations in a clay particle

Nano clays can be classified by arrangement of octahedral and tetrahedral sheets. TO layers with the ratio of 1:1 indicates the clay mineral having one tetrahedral and one octahedral sheet per layer (trioctahedral), while TOT layers with 2:1 ratio show the clay mineral having two tetrahedral and one octahedral sheet per layer (dioctahedral). Kaolinite clay minerals composed of TO layers while the other major groups of clay minerals namely Montmorillonite or Smectite, Illite and Chlorite made up of TOT layers. The existence of possible charges in tetrahedral and octahedral sheets affects the structure of clay minerals and these changes are influenced by the isomorphous substitutions. Isomorphous substitution is defined as an element of replacement in the clay particle without altering chemical structure reported by Tournassat and Steefel (2015) as shown in Fig. 1.

Compensating cations such as Al^{3+} , Mg^{2+} , K^+ , and Cu^{2+} in the clay particle is held by the negatively charged surface of clay. This phenomenon is called cation exchange capacity anticipated by the characteristic of the soil containing clay minerals. The clay would normally have a negative charge due to the isomorphous substitution by replacing silica cation with aluminium cation. Cation exchange capacity is useful in measuring fertility of the soil and allowing cation contamination-free in ground water (Inshakova and Inshakov, 2017).

2.1.2 Silica dioxide

Siliceous sand is an important source of nano silica and it is observed to be in crystalline arrangement. Silica is composed of silicon bonded with oxygen in tetrahedral manner as shown in Fig. 2, leading to a giant covalent structure. The sudden peak in 2θ scale starting from 14° to 30° indicates that the disorder arrangement of silica particles due to the amorphous nature of silica. The 2θ scale ranging from 10° to 35° is the typical diffraction band for nano silica particles that validate the characteristics of silica (Mushtaq et al., 2018).

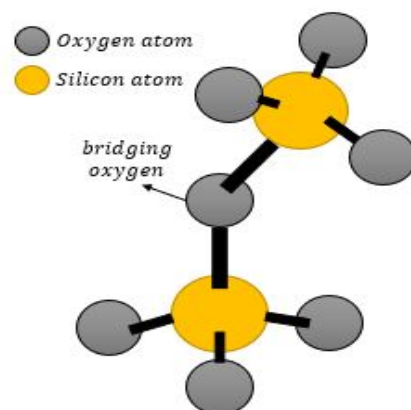


Fig. 2: Schematic representation of silica oxide structure

2.1.3 Titanium oxide

According to Raj et al. (2007), titanium dioxide appears to be amorphous if it is prepared below than 350 °C. The initiation of tetragonal crystalline structure of anatase phase occurs at temperature above 350°C. They showed in their results the common XRD pattern corresponds to titanium dioxide with the peaks depict the anatase phase. Typical diffraction at 25° and 47° for the anatase phase (Zhang et al., 2002). Fig. 3 depicts the schematic structure of anatase phase.

It is reported that rutile phase starts to form at temperature above 800 – 900 °C. The structure of rutile phase is shown by the Figure 4. It is said to be the stable phase at high temperatures, having the same structure as anatase phase. They also reported that XRD analysis has confirmed that anatase phase is the ideal growth of orientation and its intensities increase as temperature increases.

2.2 Surface morphology and particle size

2.2.1 Nano clay

Nano clays are observed to be of irregular shapes and wide range in sizes under scanning electron microscope (SEM). Collectively, SEM images depict that nano clays contain porous particles which could retain much amount of polar solvents such as water (Floody et.al, 2010).

Montmorillonite came from bentonite is composed of 2:1 layer structure portrays a larger aggregation as compared to hectorite and kaolinite due to consisting more elements in its layer. The elements involved are oxygen, sodium, magnesium, aluminium, silicone and calcium.

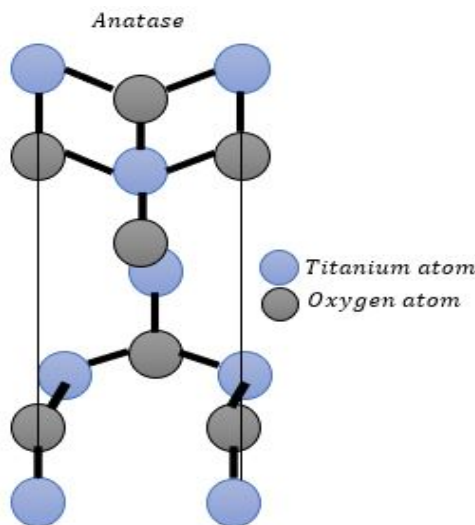


Fig. 3: Schematic structure of anatase phase titanium oxide

This results in larger in size particularly average diameter. Hectorite is composed of 2:1 layer structure is viewed to be soft and white in colour clay mineral. The aggregates of hectorite are much smaller due to lesser presence of elements in its layer. The elements are oxygen, sodium, magnesium and silicone. The average diameter appears to be few nanometres smaller than montmorillonite clay particle.

Kaolinite is a 1:1 type of layered clay mineral, consisting of oxygen, aluminium, silicone and iron elements. The average diameter of kaolinite is smaller than montmorillonite and hectorite and the aggregation of kaolinite is low. By taking into consideration of the aggregation factor and average hydrodynamic diameter, it can be deduced that smaller aggregation factor along with smaller average hydrodynamic diameter indicate greater stability of the clay mineral in water. The order of stability magnitude of these clay minerals can be expressed by the following relationship:

$$\text{kaolinite} > \text{hectorite} > \text{montmorillonite}$$

2.2.2 Silica dioxide

Microscopic analysis shows that siliceous sand is in crystalline structure with uniform surface area. Average diameter of particle of the siliceous sand is larger and its surface area is smaller as compared with silica. According to Ishak et.al (2010), silica has a non-uniform shape, appearing to be amorphous. Its particle size is revealed to be much smaller as it is extracted from the siliceous sand by means of precipitation method.

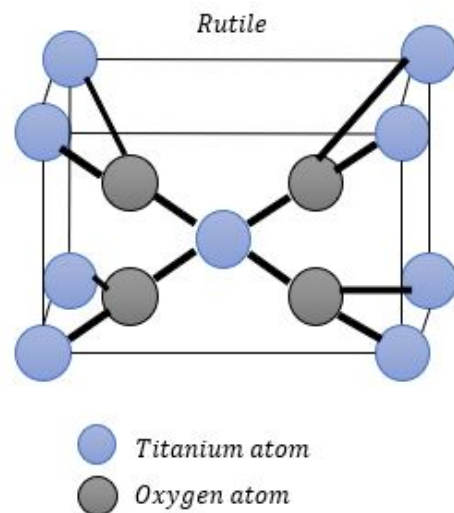


Fig. 4: Schematic diagram of rutile phase titanium oxide

2.2.3 Titanium oxide

Electron micrographs revealed that these titanium oxide nanoparticles are in anatase phase as they portrayed tetragonal anatase structure. It is (supported by study done by Verma et.al (2018), who's showed that the titanium oxide nanoparticles are indefinite shape. The particles' size appeared to be smaller as time increases when being compared to bulk titanium dioxide nanoparticles. As time increases, the hydrodynamic diameter happened to decrease. This conclude that the titanium oxide nanoparticles are much more stable in water when the particles are milled for hours.

2.3 Functional Groups and Chemical Bonds

2.3.1 Nano clay

Based on report by Floody et.al (2010), the structure of nano clays before and after peroxide treatment illustrate slight changes in FTIR spectra for the adsorption bands due to changes in organic contents. The purpose of peroxide treatment is to remove the organic content partially.

The absorption bands of nano clay either before or after peroxide treatment depict that nano clays are complex molecules as they have more than five absorption bands. It is indicated by the typical bands that show the presence of quartz mineral is below 1000 cm^{-1} due to the silicon and oxygen bonding (Nayak and Singh, 2007). The broad band between 1650 cm^{-1} to 3300 cm^{-1} specifies the hydration of water, thus leading to formation of hydrous silicates. The common occurrence of hydroxy linkage (-OH) is at about 3500 cm^{-1} , thus nano clays owning hydrous nature. Other major groups of clays are also assigned at specified bands according to the structural formula.

2.3.2 Silica dioxide

The silica before and after hexamethyldisilane (HMDS) modification illustrate slight changes in FTIR spectra for the absorption bands due to changes in organic contents. HMDS is an organosilicone compound that aims to elevate the organic matter content and preparing silica with hydrophobic properties.

The absorption bands of nano silica either before or after surface alteration depict that nano silica is a complex molecule as it has more than five absorption bands. The peak band at wavelength of 1100 cm^{-1}

portrays the main bonded elements which is O-Si-O. The broad band indicates the water absorption.

2.3.3 Titanium oxide

Based on FTIR results reported by Kanna and Wongnawa, (2008), it can be deduced that titanium oxide nanoparticles are complex molecules. The broad band between 1700 cm^{-1} and 3200 cm^{-1} depicts the stretching and bending region of hydroxyl group and amine group. The band with wavelength of 3600 cm^{-1} is assigned for O-H vibration mode of Ti-OH group. The linkage of Ti-OH is very strong and only can be broken at really high temperatures. Absorption band below 800 cm^{-1} is a region for titanium and oxygen bonding. Water molecule and ammonium ion are present based on the FTIR spectra.

3.0 Application of nanoparticles

3.1 Nano clays in food packaging

One of the essential properties of nano clay is thermal barrier property. Thermal barrier characteristic is defined as the ability to resist heat and elevated temperatures. Current development of nano clays is revealed to be substantially used and studied in polymer nanocomposites, revealing an increment in heat stability and flame retardation. The advantage of higher heat stability allows nano clays to be used as additives in manufacturing polymers with low thermic expansion (Uddin, 2008). Recent researches depict that nano clays are developed in producing commercially applicable polymer nanocomposites with modified thermal barrier and strength properties specifically in food industry.

Common food packaging material is made up from non-biodegradable materials, leading to an increased in environment pollution. The plastics are decomposed by microorganisms, resulting in diseases causation and harmful gases production. The production of plastics involves the combustion of fossil fuels in which yields a large amount of carbon dioxide, a greenhouse gas released to the atmosphere. Along with the environmental pollution caused by the traditional plastics, they exhibit poor thermal-barrier and mechanical properties (Sozer and Kokini, 2008). Addition of inorganic particles such as nano clays in packaging material gives result in increasing the biodegradability of the packaging material. This provides assurance of food safety and is considered environmentally friendly solution since it reduces the

usage of plastics. One of the polymers in plastic industry is zein, derived from corn protein is treated with stable hydrous silicate clay complexes. The typical clay mineral used is montmorillonite.

The polymer matrices are filled with clay layers to enhance their strength and heat permeability. Quality of food is maintained during storage and transportation with these functional properties. Presence of nano clays reduces the thermal- expansion factor of polymer composites ranging from 25 to 35 ppm/°C. Hence, thermal stability is a significant factor in food packaging application.

3.2 Silica dioxide nanoparticles in lubricants oil

Silica owns outstanding mechanical property including tensile strength, elasticity and large surface area. Mechanical property refers to the capability of a material to withstand upon the application of forces. Silica is widely used as additives in lubricant oils in machineries and motorised vehicles. Nano-lubricants are extensively used to reduce the friction, heat and wear between mechanical components (López et. al, 2015). Silica has a high ratio of surface area per volume, providing a large phase boundary to improve interaction of the surface material.

Engineered silica is synthesised by sol-gel method to modify size and surface properties by inserting hydrophobic chains and covalent binding with alkyl chain onto the surface of silica nanoparticles (López et. al, 2015). These help to prevent disorder arrangement of silica particles and enhance the particle distribution in solutions respectively. Another technique to minimise the aggregation of silica nanoparticles in the base oils is by addition of surfactants. Surfactants aid in uniform particles distribution in lubricants. The tribological property of silica nanoparticles is superior corresponds to the size of nanoparticles ranging from 55 to 60 nm. Tribology is the study of interacting surfaces with relative motion.

Contributing factors on the addition of silica nanoparticles in lubricant base oils include the availability of silica in the market, reduction in prices of silica and ease of silica nanoparticles synthesisation method.

3.3 Titanium oxide as antimicrobial agent

Metallic nanoparticles are thoroughly revealed as potential antimicrobials (Swaminathan and Sharma, 2019). They own toxicological property in

encountering microbes or microorganisms (Musee et. al, 2011). Toxicology is the study of the adverse effects on living organisms. The interaction of engineered nanoparticles and microbes depends on various factors such as particles' size, surface area and pH. Antimicrobial activity is influenced by the toxicity mechanism of nanoparticles towards microorganisms.

Titanium oxide nanoparticles are used as antimicrobial agent in wastewater treatment plants. One of the properties influencing the antimicrobial activity is large surface area per volume ratio of nanoparticles, broadening the interfacial of titanium oxide nanoparticles and harmful microbes. Titanium oxide nanoparticles reported to usefully killing *E. coli*, a type of bacteria typically found in environment and humans' intestines (Swaminathan and Sharma, 2019). They react with protein that contains sulphur, leading to inhibition of enzyme functionalities. Besides that, titanium oxide nanoparticles are used as fillers in health-related products such as bandages and band aids to prevent infection during the process of healing.

Titanium oxide nanoparticles possess greater stability in aqueous media. Green synthesisation of the nanoparticles from various sources aims to speed up the synthesis rate at any parameters, modify size and shape as well (Nadeem, 2018). Various plant species have been used to produce several shapes of titanium oxide nanoparticles. A component in leaves of the plant species namely metabolites can reduce the titanium oxide into nanoparticles within 5 to 7 hours, thus the growth stability is then achieved.

4.0 Conclusion

In recent years, development of nanoparticles has been extensively explored to be used as additives in materials for various commercial and domestic applications. Both physical and chemical properties possessed by nanoparticles can be utilised for performance alteration. Properties include crystallographic structure, surface morphology, particle sizes and chemical bonds. These properties can be analysed by standard characterisation methods such as scanning electron microscopy, X-ray diffraction and Fourier-transform infrared spectroscopy.

All these approaches leading to intensive research in modifying existing materials with desired outcomes. Nano clays, silica oxide and titanium oxide have been investigated for their thermal-barrier properties, mechanical properties and toxicological properties respectively. Nano clays are used in food packaging,

silica oxide as additives in lubricant base oils and titanium oxide as antimicrobial agent.

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