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Advanced ceramics and relevant polymers for environmental and biomedical applications

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ABSTRACT
Ceramics result from combinations and structural arrangements of inorganic substrates for metals and nonmetals. They bind covalently forming ceramic with distinctive properties. Advanced ceramics can be applied in progressive applications. They comprise advanced heat engines for communication and energy transmission. They are developing among the required materials for advanced technologies. Advanced ceramics are getting along modern technological applications. Researches and studies focus on enhancing and optimizing the desired properties. They are trying to overcome some disadvantages such as brittleness and poor mechanical properties. Polymers play an important role in either forming ceramics or blending with them to form efficient composites. Some polymers are classified as inorganic and organic materials such as polysilazanes. They consist of silicon, nitrogen, hydrogen and carbon in certain cases. Polysilazanes act as precursors to SiO_2, Si_3N_4 and SiC ceramics. Perceramic polymers are pyrolyzed polymeric materials in an inert atmosphere producing ceramic materials. Ceramics can be applied in the absence or the presence of polymers in various fields. They comprise wear related, environmental and electrical applications as well. Bioceramics and biopolymers were used as implants in orthopaedics. Zirconia based ceramics act as successful materials to be applied in dental applications.
Keywords: *ceramic, clay, polymer, coating, polysilazanes, medical applications.*

1. INTRODUCTION

The word (ceramic) seems to be derived from the word "keramos". It is a Greek word that means burned clay. The word keramos itself has Indo-European roots. It looks to affiliate to Sanskrit word *Car or Cra*. It means cook and viewed as the origin of nominating ceramic [1-3]. Ceramics are correlated with clay-based products. Among the well-known examples of these products, we can mention bricks, pottery and tableware. Some natural minerals such as clay, quartz, bauxite and feldspar are employed to produce these ceramic substrates. The first known ceramics possessed clay as a major ingredient. They were constructed by firing the clay substrate. Tiles, porcelain, sanitary ware and bricks are among the famous ceramic products. They are based on the potter's clay.

Wet-chemical routes such as co-precipitation, sol-gel, spray dry and freeze-dry are used to manufacture advanced ceramic powders. The aforementioned powders contain submicron size and/or nano size, narrow size distribution without particle agglomerates. Meanwhile, these procedures need long processing time, expensive chemicals and certain instruments. Several variations may appear upon comparing advanced ceramics and conventional ones [4,5].

They may include the high-mechanical strength, comparable fracture toughness, dielectric, magnetic and optical properties beside wear resistance. In addition to the "traditional ceramics", there is a novel category of ceramics, known as the "advanced ceramics". They became popular products in the twentieth century. Advanced ceramics; also known as fine ceramics possess high value-added inorganic materials. The latter are created from high purity synthetic powders. They are able to control microstructure and properties. Such advanced ceramics are valorized by their beneficial characteristics, high chemical purity and careful processing. These substances were developed for structural and electronic implications [6-8]. Advanced ceramics have been applied to fabricate improved materials with complex requirements. These materials show high performance. Further applications may include the nuclear industry and satellites with sensors, insulators, inserts and valves [9,10]. In addition, such medical implications can arise. They require high accuracy such as biocompatible implants, including dental prosthesis, bone replacement and cardiac valves [11-13].

Advanced ceramics play an important role in technological domains. This may comprise environment, transport, communication and information technology [14]. They provide a promising behavior which is not easily offered by traditional ceramics [15]. The used term to define this kind of ceramics changes from a place to another. Japanese literature nominates it as *fine* ceramics. Meanwhile, American context refers to it as *advanced* ceramics. The European literature mentions it frequently as *technical* ceramics. In England, the term *technical ceramics* is classified into *functional ceramics* and *structural* ones. The first term is applied in mechanical constituents and electronic applications [16].

They are known as electronic ceramics or electroceramics. *Structural* ceramics are the class of ceramics which focuses primarily on mechanical properties such as hardness, toughness and wear resistance. Advanced ceramics have distinctive features by which these surpass the conventional ceramics. These features comprise the low density, hardness, low coefficient of thermal expansion and high processing temperatures. The ceramic products exceed their corresponding metallic ones in cost, durability and abundance. The required resources to produce metallic materials diminish. Hence, the manufacturers look for ceramic alternatives. Bioceramics represent a class of ceramics that are used inside the human body. They comprise hips and bone transplants. One can use these materials as supports for directed delivery of just enough doses of medicines. Bioceramics show appropriate mechanical strength. Consequently, they can be selected as ideal materials for such applications. They support in healing some affected sites in the body. These ceramics are inert with regard to body fluids [17,18].

It is worthy to mention that ceramics supported in advancing the means of the transport industry. The sparkplugs made of alumina (Al_2O_3) ceramic prove that the vehicles would not be progressed in the absence of refractories. In spite of the substantial role of ceramics in various applications with their unique properties, but these materials compete with cheap metals, alloys and composites [16].

Thus some obstacles encounter applying the advanced ceramics. They include the relatively high costs and lack of maintenance. Various researches were enrolled to overcome these drawbacks by enhancing the properties and designing efficient preparation procedures [19,20].

2. PROPERTIES OF ADVANCED CERAMICS

Advanced ceramics are generated from three major kinds of materials. They are oxides, non-oxides such as carbides, and nitrides. Japan had the lead for many years in producing advanced ceramics with elevated exports followed by North America. They are mainly electronic ceramics. This progress is due to the partnership between companies in researches and development [16,18]. Structural ceramics were noticeably improved mainly in enhancing the fracture toughness. They showed prominent fracture toughness more than glass and less steel. Among the advanced ceramics, zirconia (ZrO_2) is referred.

The word zirconium is derived from the Persian (Zargun) which means a golden color. It exhibits toughness of about 15 MPa. $m^{1/2}$. This value exceeds that of tungsten carbide cobalt (WC-Co) cermet and cast iron. Such improvement in the resistance to contact stress and handling damage led to defining durability when compared to metals and WC-Co cermets. Various ceramics exhibit strengths less than 345 MPa. Recently, advanced ceramics such as silicon nitride (Si_3N_4) and toughened zirconia (ZrO_2) are commercially available. They exhibit strengths above 690 MPa [21].

2.1. Polymer derived ceramics.

Silicon-based polymer derived ceramics were prepared since the second half of the twentieth century. Their synthesis was carried out by heating organosilicon polymers [22]. They are known as precursor ceramics. Some researches clarified how the polymer can be transformed into ceramic. Among those polymers; polysilazanes, polysiloxanes, and polycarbosilanes can be mentioned to form silicon nitride-silicon carbide ceramic fibers. Researches followed up to showed employing the thermolysis of polycarbosilanes to form silicon carbide ceramics. These polymers as precursors comprise inorganic/organometallic substrates. They supply ceramics with unique chemical forms. These entities resemble thermally treated nanostructures. Polymer-derived ceramics have favorable oxidation and creep resistance even at high temperatures. Their most common kinds are in the binary, ternary and quaternary categories. They comprise Si_3N_4, SiC, BN, SiCN, SiCO, SiCNO, SiBCN and SiAlCO [23,24]. The conventional method to prepare Ceramics are synthesized traditionally through powder technology. Sintering additives are needed to be introduced while to provide desired properties. Upon following the path of polymer-derived ceramics, ceramic fibers, layers, yarns or composites may result without applying the powder technology. Preceramic polymers may be formed by utilizing conventional polymer forming methods. The latter comprise injection molding, extrusion and coating. The preceramic polymers may be changed to ceramic ingredients by heating. High temperature are able to merge the polymeric components to produce a ceramic. Polymer derived silicon boron carbonitrides (SiBCN) exhibit higher thermal, chemical and mechanical (creep) stability than their boron-free analogues. This occurs in an inert atmosphere at 2000 ^{o}C. Their remarkable thermal stabilities depend on kinetics more than thermodynamic behaviors. Some structural disorders in SiBCN ceramics may lead to higher free activation energies of both crystallization and the solid-state reaction of the Si–N bond with carbon [25].

2.2. Polysilazanes as inorganic and organic polymers.

Polysilazanes are polymers that consist of Si, N, H beside C in specific cases. These polymers may be classified as either (inorganic) perhydro-polysilazanes or organo-polysilazanes or polycarbo-silazanes. Organo-polysilazanes exhibit carbon-containing groups. Such groups in the polymeric chains are methyl or vinyl ones attached to Si or N. Polysilazanes act as precursors to SiO_2, Si_3N_4 and SiC ceramics [26-29]. They can be considered as successful substrates to produce silicon-based ceramics. They may include fibers and fiber reinforced ceramic composites [30]. Utilizing polysilazanes commercially has augmented frequently over the past few years. Polysilazanes were synthesized by using an ammonolysis reaction of various dichlorosilanes and trichlorosilanes. This reaction takes place in an organic solvent in the presence of ammonia. Inorganic polysilazanes are applied in the electronics industry.

They are used as precursors for the surface coating of silicon dioxide. These coatings may be produced from dilute solutions of perhydro-polysilazanes in organic solvents. Conversion to SiO_2 is achieved by either permitting the settled polysilazane coating to crosslink or by heating in moist medium up to 250 °C to produce SiO_2. Moreover, polysilazane can be cured by ultraviolet radiation to form SiO_2. Polysilazane-derived SiO_2 coatings are able to be used in different implications. Among these applications, gas-barrier films and anticorrosion coatings for aluminum metal can be mentioned. Furthermore, SiO_2 coatings are set on the silicon wafers to manufacture semiconductors. This is performed by covering the silicon surface with a spin-coated polysilazane. This is followed by changing the coating layer of polysilazane coating to a SiO_2-based coating film [31,32].

2.3. Preceramic polymer synthesis.

Perceramic polymers are pyrolized polymeric substrates in an inert atmosphere to produce ceramic materials. The kind and structure of preceramic polymers affect the composition. This results in the formation of ceramic by different phases and a phase distribution with a microstructure. Hence, the chemical and physical behaviors of polymer derived ceramics may be controlled according to the structure of the polymeric precursor [33,34].

The effective silicon-containing polymers such as silicon carbonitrides and oxycarbides may be referred to the successful interaction between the polymeric Si and C atoms. Converting silicon-based polymer to the ceramic takes place at temperatures below 1100 °C [35,36].

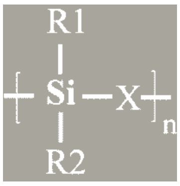

Figure. 1. The molecular structure of preceramic organosilicons.

An organosilicon polymer is a successful precursor to prepare ceramics as shown in Figure 1. For an efficient designing and enhancing of the preceramic material, certain factors have to be considered. They comprise the group (X) in the polymeric chain. (X) is a variable compound in silicon-based polymers. Poly(organosilanes) will have X=Si. Poly(organocarbosilanes) have $X=CH_2$. Poly(organosiloxanes) have X=O. Poly(organosilazanes) have X=NH and poly(organosilyl carbodiimides) with $X=[N_5C_5N]$. In addition, the entity of the attached substituents to silicon; R1 and R2 is a significant parameter.

The solubility, thermal stability and viscosity as a function of the temperature are essential characters to process the polymers. The preceramic polymer surpasses traditional ceramics by the facile and selective preparation procedure synthesis. The selectivity provides a suitable opportunity to obtain novel materials with appropriate properties. Chloro-organosilicon compounds are known starting materials to produce polysilanes, poly(carbosilanes), poly(organosilazanes), poly(borosilazanes), poly(silylcarbodiimides), poly(silsesquioxanes), poly(carbosiloxanes), and other silyl-containing polymers [37,38].

It is important for the polymers to have a high molecular weight. This supports in reducing the volatilization of low-molecular ingredients. They have to exhibit suitable rheological properties and solubility. Hence, this step facilitates the shaping stage. The organic side groups in the polymer have a role in estimating the content of carbon in the ceramic. Moreover, carbon can contribute to changing mechanical and high-temperature properties such as resistance to crystallization and oxidation.

The high carbon content in polymers-loaded with SiCO and SiCN ceramics shows a high resistance with respect to crystallization and decomposition [39].

3. SOME APPLICATIONS OF ADVANCED CERAMICS

Advanced ceramics showed progressive achievements under competitive circumstances. They are present in various implications including environmental, engineering and biomedical applications. The most popular ceramics are alumina, zirconia, silicon nitride, silicon carbide and ferrite.

3.1. Wear related applications.

Advanced ceramics exceed cemented carbides in cutting tool application. This is correlated to their hardness and strength. They are capable of being used in high-speed and efficient machining [40]. A tool with specific properties is required for finishing operations or metal machining. It must have high fracture toughness and thermal shock resistance with chemical stability [14].

In cutting implications, it is important to enhance the life and the speed of the cutting tool [16]. During cutting of hard metals such as cast iron and high-temperature superalloys, high temperatures are developed at the tool work piece interface, with decreasing tool life and cutting speed. Thus, the use of advanced ceramics in cutting applications is more cost effective owing to the high removal rate during cutting. This feature increases the production rates, decreases flank wear of the tool tips and gives the capability to cut difficult-to-machine materials. The suitable machining temperatures for nickel based superalloys are about 1200 °C. They can be provided by ceramic cutting tools [41].

Conventional WC-Co shows endurance at high temperatures. This limits the cutting speed to 121.6 m/min [16]. However, utilizing silicon nitride (Si_3N_4) showed cutting speeds at 1520 m/min with a depth cut of 5 mm and feed rate of 0.4 mm per revolution. The operating temperatures is kept up to 1100 °C [21]. Alumina (Al_2O_3) exhibits a high performance ceramic in a low cost. It can be produced in huge amounts. Alumina is applied in roughing and finishing applications of iron [42]. Si_3N_4 shows high fracture toughness. It is used in machining applications. Silicon carbide (SiC) is a commonly used ceramic, commercially. They show high wear resistance and high temperature strength when compared to Al_2O_3 and Si_3N_4. Al_2O_3 seems to be cheaper than SiC. The latter shows a feed rate of 0.4 mm per revolution with operating temperatures of up to 1100 °C [21]. SiC whisker-reinforced alumina ($SiCw/Al_2O_3$) are commonly used ceramic composites as cutting tools. They are applied commercially in machining difficult materials such as Ni-based superalloys in gas turbine industry.

Moreover, they act as wear components in the ceramic/metal hybrid tooling and dies in the canning industry for cupping, drawing and can necking. The advance ceramics involve in the finishing of hard top machine materials after being roughened with carbide materials. Such substrates possess fine grain size lower 100 nm. This supports in providing fine cutting edges with an enhanced tool wear resistance [42].

3.2. Ceramic coatings.

Organopolysilazanes are able to form ceramic coatings at high temperatures. Si_3N_4 based composites compose coatings from organopolysilazanes [43]. Some sources of energy can assist in the coating process. Silicon carbide can form a successful coating with microwave [44]. They are able to seal oxide fuel cells and electronic adhesives to adhere circuit chips to carriers. Methyl hydrido polysilazane with Al_2O_3 and glycidoxypropyl trimethoxysilane is pasted to stick an electronic component with the required substrate. The silicon-based device ingredient is heated to 400 °C to change the polysilazane into a ceramic [45,46]. Ceramic coatings are applied commercially in the form of coatings based on organopolysilazanes. The surfaces of graphite sheets were coated with a polysilazane layer [47]. This was followed by pyrolysis in atmosphere to 1000 °C. Upon heating the coated sample above 1400 °C, a β-SiC coating was produced.

3.3. Clay-polymer composites for environmental applications.

Clay denotes to ceramic materials. It can be mixed with organic polymers or used separately to produce composites. They may be utilized in environmental applications comprising adsorption and heavy metal removal [48-50]. Clays participate in different fields like producing polymers nanocomposites. Natural clays are present in nature massively at low cost.

This allows them to be applied as successful adsorbents to get rid of toxic materials from waste water. These ceramics exhibit tetrahedral and octahedral sheets. They act vitally to trap pollutants from irrigation water in the soil. There are many kind of clays such as montmorillonite, smectite, kaolinite and illite. They can be found in sedimentary rocks. The high surface area of the fine particles provides clays potential adsorption ability towards different organic dyes, metals or other contaminants [51-53]. Natural clay minerals are valid at cheap prices. Hence, they can be considered as competent adsorbents to eliminate toxic materials from wastewater.

Clay-organic interaction has been discussed. Organic moieties can be adsorbed on the clay surface via ion-dipole forces. Moreover, it is able to complex with a counter ion of the clay. It can be subjected to cationic or anionic exchange with the original counter ions. Ceramic is formed when some inorganic and non-metallic oxide; nitride or carbide materials are fired. Different additives may be introduced to the ceramic before or after firing to improve the properties. Ceramic filters are produced commercially at relatively low costs. Hydrophobic clay alumina capillary filters were utilized to desalinate sea water [52]. They were synthesized from silica-based ceramic fibers of waste rice husk. Polymeric based filters have some disadvantages when compared with ceramic based ones.

The polymeric filters cannot be used at high temperature or hard chemical media. So, ceramic filters surpass some polymeric ones. This may be referred to their high thermal stabilities beside their non-swelling features [54]. Consumed polystyrene is present in large amounts as a solid waste among the used scrap. Expanded polystyrene (EPS) is a packaging material and can be used insulator. EPS is a foamy tough product. It is listed as one of the main plastic wastes. It exhibits low density with chemical and thermal resistances [55].

EPS encouraged scientists and manufactures to be recycled after being present in the environment as a main polymeric waste [56]. EPS is almost a hydrophobic spherical granule. It contains about 2% polystyrene and 98% as air [57,58]. It can be processed as a walling material in construction applications. Some drawbacks for EPS may arise such as being a non-biodegradable polymer [59]. Hence, it is beneficial to add EPS to other materials such as ceramics to form composites in an attempt to reduce their burden on the environment.

Ceramic membranes based on clay and expanded showed potency in adsorbing methylene blue (MB) from water. MB acted as a model dye for those to be in waste water. This can be illustrated in Figure 2.

3.4. Bioceramics and biopolymers.

Biomaterials are those substrates that interact with human bodies. They are used for treating, enhancing or replacing some tissues or organs in humans. Implants are the class of employed biomaterials in medical devices for orthopaedics [60]. Ceramics can be used in total replacement for more than two decades ago. The commonly used ceramics in this domain are alumina and zirconia. They replaced polyethylene in hip implantation. Alumina ceramics were favored due to their thermo-mechanical properties representing high hardness and wear resistance. [61].

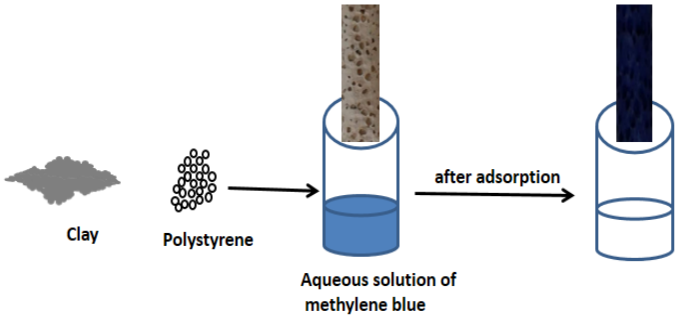

Figure 2. A scheme showing the absorption process from water by the ceramic based membrane.

Zirconia competed alumina as orthopaedics [62]. They are applied in producing femoral heads for total hip replacements. This is due to their high strength and toughness. Thereafter, they are able to lower the risk of fracture. Zirconia is present in 3 structures. They are monoclinic, cubic and tetragonal [63].

Pure zirconia is monoclinic at 25 °C. It is a stable phase up to 1170 °C. It converts to tetragonal structure at higher temperatures. This is followed by a cubic phase transformation at 2370 °C. The phase transformation is accompanied by a change in the volume. The mechanical properties will vary with generating some cracks [64]. Some deformations arose in tetragonal Zirconia mainly in hip prostheses. This was because of a rupture risk with intense cracking [65].

There are many polymers applied as biopolymers. In the second half of the last century, polytetrafluoroethylene (PTFE) was used as an acetabular constituent [66]. It was implanted with a stainless steel femoral component. This polymer is hydrophobic with high thermal stability. PTFE showed to be inert inside the body with a low frictional behavior [67]. However, PTFE exhibited an inappropriate wear feature in hip replacement prostheses. [68]. This character led to a tissue reaction with forming granuloma.

PTFE is limited in such load bearing implications. Ultra high molecular weight polyethylene (UHMWPE) then contributed to forming the acetabular cups. They were developed and proceeded to be used as promising materials. UHMWPE is prepared as a powder. It is formed of very long chains of polyethylene. It gains strength from its length [70,71]. The powder is introduced to its final implant form. This is performed by a direct compression molding technique. Any change that may arise during the preparation procedure may cause some alterations in the physical and mechanical properties of the polymeric product [72].

Any surface roughness of the implants may influence the wear rate after removing the machining marks [73]. Any debris in the polymeric socket may give rise to undesirable biological reactions. This will be followed by osteolysis. Hence, this disadvantage has to be avoided as possible.

3.5. Advanced dental ceramics.

The dental materials have been progressed extensively throughout the past years. Their technologies allowed new materials to participate in dentistry such as zirconia-based ceramics. These ceramics exhibit significant mechanical properties. This can be correlated to the tetragonal to monoclinic phase transformation. By this transformation, the induced external stresses increase.

The aforementioned stress is like grinding, cooling and impact. The transformation stress is accompanied by an increase of volume and gives rise to compressive stresses. Transformation toughening takes place as the zirconia particles are in the metastable tetragonal form. This stability depends mainly on the composition, size and the shape of zirconia particles [74]. Moreover, the mentioned toughening is not the sole technique for zirconia-based ceramics. Other mechanism such as microcrack toughening, contact shielding and crack deflection participate in the toughening of the ceramic [75-77].

In-Ceram Zirconia (IZ) and DC Zirkon (DZ) IZ and DZ are the expression of two different approaches of applying zirconia in dentistry. IZ has been promoted by adding CeO_2 partially stabilized zirconia to In-Ceram Alumina (IA).

This approach tries to facilitate utilizing the partially-sintered glass-infiltrated alumina. The perfect milling of the dry pressed ceramic contributes to providing an efficient ceramic with acceptable mechanical properties.

4. CONCLUSIONS

Ceramics possess a structure of inorganic materials for metals and nonmetals. They interact via covalent bonds. Ceramic materials are clay-based products such as bricks, pottery and table ware. They are based on naturally abundant matters as quartz, feldspar and clay. Ceramics result from firing clays.

Natural clays are abundant at low prices. Advanced ceramics may be used in engineering and energy transmission applications. In addition, ceramics are favored as cutting tools in engineering applications. Polymers are major components in producing ceramics. These polymers diverse between inorganic and organic substrates. They are based on Si, N, H and probable carbon for some polymers.

Perceramic polymers are polymeric materials that have to be heated in the absence of oxygen to form ceramics. Organo-polysilazanes can produce ceramic coatings at elevated temperatures. Silicon carbide whisker-reinforced alumina form composites. They are commonly utilized as cutting tools. They are applied commercially in machining difficult materials such as Ni-based alloys in manufacturing machinery parts. Ceramics may be used in the absence or the presence of polymer in many domains such as environmental and electrical applications.

Clay can form hybrid membranes and filters with organic polymers such as expanded polystyrene. They showed successful efficiencies in environmental applications.

They were able to adsorb dyes from water. Bioceramics and biopolymers were applied to treat or replace some tissues in human bodies. They were implanted in medical devices for orthopaedics. Zirconia based ceramics are considered as promising materials to be applied in dentistry.

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