

Review Article

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Polymeric Nanocomposites

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Abstract

Polymer nanocomposites have become a quickly growing area of study, fueling the advancement of sophisticated materials in recent years. Adding nanoparticles to a polymer matrix greatly improves the characteristics of the resulting nanocomposites. These improvements play a crucial role in a wide range of applications, including dental restorations, biosensors, food packaging, electronic devices, and various biomedical uses. This review offers a thorough examination of various techniques for synthesizing polymer-based nanocomposites, such as melt intercalation, sol-gel processes, in situ polymerization, and emulsion techniques. Moreover, it is essential to characterize these nanocomposites to comprehend their mechanical properties, structure, and morphology. The removal of textile dyes from wastewater using advanced polymer/clay composites. It provides an in-depth analysis of the chemical and physical properties of these composites, emphasizing how the combination of polymers and clays creates a synergistic effect that significantly improves the efficiency of dye removal. The structural versatility of the composites, derived from the interaction between the layered clay sheets and the flexible polymer matrices, is detailed, showcasing their enhanced adsorption capacity and catalytic properties for wastewater treatment. This study outlines the key functional groups present in both polymers and clays, which are crucial for binding and degrading a wide range of dyes, including acidic, basic, and reactive dyes. The role of specific interactions, such as hydrogen bonding, ion exchange, and electrostatic attractions between the dye molecules and the composite surface, is highlighted. This study investigates the advanced characterization techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA), to help researchers assess the morphological, structural, and thermal properties of the composites, aligning these features with their potential application in dye removal. The primary mechanisms involved in the dye removal process, such as adsorption, photocatalytic degradation, and catalytic reduction. It also provides an overview of the kinetic and thermodynamic models commonly used to describe the adsorption processes in polymer/clay composites. The environmental and operational factors influencing the efficiency of dye removal, such as pH, temperature, and composite dosage, are analyzed in detail, offering practical insights for optimizing performance under various wastewater conditions.

Keywords: Polymer; Nanocomposite; Dye; Textile; Waste; Dentistry

Introduction

Polymeric nanoparticles are prepared through dispersing performed polymers using different methods like, solvent evaporation, nanoprecipitation, salting-out, and supercritical fluid technology [1]. Polymer matrices are widely used due to their lightweight properties, ease of production and ductile nature. Polymer systems face some problems such as modulus and strength are lower than metals and ceramics. The best practice to improve the properties of the polymer system is the addition of particles such as platelets, whiskers and fibers to form a composite with the interacting elements of the matrix and other materials [2]. Polymer nanocomposite matrices consist primarily of a polymer matrix and a dispersive phase at the nanometric scale in one dimension. Typically, incorporating fillers at a weight percentage of 10–40% substantially enhances the mechanical properties of the resulting matrix [3].

removal of textile dyes from wastewater using advanced polymer/clay composites. It provides an in-depth analysis of the chemical and physical properties of these composites, emphasizing how the combination of polymers and clays creates a synergistic effect that significantly improves the efficiency of dye removal. The structural versatility of the composites, derived from the interaction between the layered clay sheets and the flexible polymer matrices, is detailed, showcasing their enhanced adsorption capacity and catalytic properties for wastewater treatment. The review outlines the key functional groups present in both polymers and clays, which are crucial for binding and degrading a wide range of dyes, including acidic, basic, and reactive dyes. The role of specific interactions, such as hydrogen bonding, ion exchange, and electrostatic attractions between the dye molecules and the composite surface, is highlighted. Moreover, the selection criteria for different types of clays such as montmorillonite, kaolinite, and bentonite and their modifications are examined to demonstrate how structural and surface modifications can further improve their performance in composite materials.

Polymer nanocomposite Nanocomposite (NC) are define as solid and colloidal particles of macromolecular substances ranging in dimension 100 nm [4] There are several application areas which led to the investigation of different nanocom-

posite [5]. Organic NPs, lipid-based NPs and metal-based NPs [6]. Synthetic materials and synthetic materials are used for the preparation of polymeric NPs [7]. Polymers are used as synthetic materials due to the useful properties, good biocompatibility, biodegradability, ease of preparation and design, chemical diversity, and attractive biological properties [8]. Most polymeric Nanocomposites (PNC) were recognized as biodegradable and biocompatible over the accomplished few decades [9]. They used to deliver drugs, proteins, peptides, and antigens also targeted to particular organ DNA transporters in gene therapy [7]. Energy sectors, automobile industry, in aerospace and military industry are preferred area in future [8]. Protein can help to synthesis polymers from, milk proteins and gelatin; polysaccharides such as starch, chitosan and sodium alginate [9]; and synthetic polymers such as poly methyl methacrylate, poly(cyanoacrylate) PCA, polycaprolactone (PCL), poly (lactic acid) (PLA), poly (D, L-glycolic acid) (PGA), and their copolymer of poly (lactideco-glycolide) PLGA are used in preparing nanocomposite systems [10].

Polymer nanocomposites NPs are classified depending on their morphology, size and chemical prop NPs are classified depending on their morphology, size and chemical properties. It was categorized based on physical and chemical characteristics, some of the well-known classes of NPs are [1,11] carbon-based nanoparticles (NPs), metal-based NPs, ceramics NPs, semiconductor, polymer NPs [1].

Classification based on the dimension of nanofillers showed zero-dimensional nanofillers, for example, possess nano-scale dimensions in all directions and can be in the form of nanoparticles that are crystalline, amorphous, ceramic, or metallic in nature [12,13]. One-dimensional nanofillers having nano range dimension along just one direction such as nanowires and nanotubes [12]. They usually have needle-like forms such as nanoplatelets, nanorods, Nano clays and nanosheets [14] with conductive nanocomposites and stretches based on alginate and silver nanowires to create electronic devices. Two-dimensional nanofillers carbon nanotubes are the best possible examples [14].

It can also include nanofibers, nanorods and nanowhiskers

[12] synthesized polyacrylamide/montmorillonite nanocomposites.

Metal sulfides such as CdS, ZnS, are embedded in polymer materials [15-16]. There can be many methods for creating such nanocomposites, but the most important is the hydrothermal and thermal decomposition method [20] of synthesized zinc sulfide sodium carboxymethyl cellulose nanocomposite film [15-18]. Metal hydroxide nanocomposites are well known for their flame-retardant properties [19-21]. The main nanofillers used are magnesium and aluminum hydroxides, usually in the form of wires and fibers [21]. The polymer matrices used can be poly (vinyl chloride), elastomers, phenolic compounds and unsaturated polyesters [22]. As the temperature increases, endothermic decomposition of metal hydroxides begins [23]. They thus make it possible to separate heat treatment into materials. The support of such charges on the surface makes the barrier of the ceramic or vitreous layer [14,17,21]. Metal Oxide can be synthesized using different methods such as hydrothermal methods, solgel methods, sonochemical approaches and coprecipitation methods. Examples of nanofillers include silica, ferric oxide, titanium oxide and copper oxide [24]. They synthesized an electrochromic material consisting of polyaniline-based nanofibers covering nanorods of antimony-doped tin oxide and titanium oxide [4,25]. D) Silicate powder is prepared with alcohol such as [26,27] ethanol, ammonium hydroxide, water mixed with water and hot air and then add different dispersions and dispersions [28]. After separating the parts of the dispersion and silica synthesized for identification, residual silica expanded. It is treated with a silane coupling agent [26]. The clay material is resistant to transport therefore the heating effect is not seen due to the coating [29]. Synthesized iron oxide-polymer nanocomposite integrated with laminated magadiite silicate using ion exchange and synthesis method and used for oil recovery [28, 30]. The distribution, size, shape, and interaction of nanofillers within the polymer matrix significantly influence mechanical, thermal, and electrical properties [31-32]. At the nanoscale, the increased surface area of fillers leads to enhanced interfacial interactions, which can improve the dispersion and bonding between the fillers and the polymer [33]. These interactions affect properties such as tensile strength, modulus, and impact resistance. In the synthesis

of polymer nanocomposite various methods can be employed into two main classes [11]. Nanoparticle preparation methods can be divided into physical and chemical methods depending on whether chemical reactions are involved [34]. On the other hand, these systems can be divided into gas phase, liquid and solid phase [2] depending on the conditions of the reaction system [35]. The process of gas includes the process of gas heating (resistance heating, high temperature heating, plasma heating, electric heating, laser heating, electric heating, vacuum or sputtering) [36]. Liquid fraction nanoparticle synthesis methods mainly include precipitation, hydrolysis, spraying, thermal melting process (high temperature and high pressure), melting evaporation pyrolysis, redox (ambient pressure), emulsion, chemical synthesis by radiation and Sol-gel processing. Solidification methods include combustion, solid state reactions, annealing, pickling and grinding [37]. Synthesis of polymer nanocomposite by sol gel The term "sol-gel" refers to a process that includes two reaction phases: sol and gel. In this context, the "sol" is a colloidal suspension in which a solid is dispersed in a liquid. A "gel" is a cohesive network that forms between these processes. The sol-gel method is widely used to produce solids from small particles at low temperatures [7]. In this process, the most important step is the conversion of the precursors into the colloidal through hydrolysis and condensation reaction [37]. In this process, particles or fillers are dispersed in a monomer solution (called sol) that emerges from the layers of the particle. These results in the formation of an interactive network of polymers and nanoparticles (called gel) [34, 37]. Therefore, the polymer contributes to the nucleation and growth of nanomaterials [38]. This method is similar to the surface method [35-36] prepared by chitosan and salicylaldehyde in the presence of TiO₂ nanofillers to form a nanocomposite membrane [4]. The recovery of metals, excess water, solvents, heat and the use of complex substances or catalysts are the main reactions [3]. Whether it is used or not depends on the chemical nature of the metal atom and the strong resistance of the alkoxide group. The electrophilic nature of the metal atom and its ability to increase the coordination rate are the main factors [36]. In situ polymerization The process works on the principle of the absorption of the monomer solution by the platelets as they respond [34]. This is followed by the polymer-

ization of the monomer under the influence of heat, initiators or UV light. Therefore, the formation of exfoliated nanocomposites or intercalated nanocomposites takes place [39]. In situ template synthesis is another method in which the size of the platelets is controlled as a polymer matrix [40] and the platelets move in a high fluid such that the nucleation of the platelets is under the control of the polymer chains that enter the do them [40-41]. However, this method has the disadvantage of increasing the decomposition of polymer chains at high temperatures [42]. It is well known that the incorporation of clay (nanomaterials) into polymer matrices improves properties such as hardness, resistance and fire resistance. Intercalation is a top-down method that requires modification of the nanoplatelet surface for the diffusion of platelet-like nanofillers in the polymer matrix [26]. An additional strain occurs when the polymer chains diffuse into the gallery space of the layered structure. Nanoplatelets can be individually dispersed by chemical and mechanical methods [43]. The chemical process is a process, in which the nanoparticles are dispersed in the monomer, then the polymerization reaction takes place, then the nanoplatelets are dispersed in the polymer, followed by another polymerization process [2]. Nanoplatelets react with the monomer solution and polymer formation occurs between the assembled sheets through the polymerization process [44,45]. The repair method is to inject the polymer into the nanoplatelets directly by mixing the solution [45]. The polymer is dissolved in the coating and the nanoplatelets pieces react with the solvent. The two solutions are mixed and the polymer chains from the solution enter the nanoplatelets cavity and remove the solvent [46]. The relationship between the working surfaces is very important in the effectiveness of the intercalation method, as they affect the connection and the performance of the intercalated. Poor social interaction can lead to problems such as temporary or negative separation, undermining the value of the relationship [41,42].

A Case Study

Natural and synthetic clays have long been employed in wastewater treatment due to their distinct physicochemical properties, which make them versatile for a variety of environmental

applications [47]. Their widespread use, particularly in adsorption and catalytic reduction processes, has been driven by their high surface area, layer charge, and their ability to modify their structure to enhance functionality. In recent years, advancements in nanotechnology have led to the modification of clay minerals into low-dimensional materials such as nanosheets and nanotubes, increasing their utility in developing multifunctional composites for more efficient wastewater treatment. Structurally, clays exhibit a range of configurations, including 2:1 layered (such as montmorillonite), 1:1 layered elongated discontinuous octahedral sheet (such as in halloysite), and multilayered nanotubular formations [46,47]. These structural characteristics significantly influence their surface properties, reactivity, and interaction with pollutants. For instance, the 2:1 layered clay, where two tetrahedral sheets sandwich an octahedral sheet, offer a high degree of flexibility in terms of swelling and ion exchange capacity. This flexibility allows them to effectively trap pollutants between their layers, making them highly suitable for adsorption processes. Montmorillonite, a smectite mineral, is particularly favored in wastewater treatment due to its high cation exchange capacity (CEC) and large interlayer space, which facilitate the adsorption of various contaminants, including heavy metals, dyes, and organic molecules [48]. The presence of hydroxyl groups on the surface and edges of montmorillonite enhances its reactivity, allowing for both physical and chemical interactions with pollutants. These clay minerals are favored not only for their abundance but also for their ease of functionalization. By incorporating polymers, metal oxides, or other nanomaterials, clay minerals can be transformed into advanced composites that exhibit superior adsorption capacity, enhanced mechanical stability, and selective pollutant targeting. For example, the formation of polymer-clay nanocomposites allow the introduction of functional groups capable of interacting with specific contaminants, such as acidic or basic dyes, through electrostatic interactions, hydrogen bonding, or complexation mechanisms. Furthermore, the high surface area of these materials provides numerous active sites for adsorption, while the layered structure enables intercalation of pollutants into the clay galleries. This makes clays particularly effective for removing inorganic contaminants like heavy metals as well as organic pollutants such as dyes

and pharmaceutical residues from wastewater. Their tunable properties and ability to undergo various modifications make them versatile tools for tackling a wide range of environmental pollutants.

The Most Common Polymers in Wastewater Treatment

A variety of porous and layered materials, such as activated carbon, natural clays, zeolites, and metal–organic frameworks (MOFs), are commonly employed for wastewater treatment due to their low cost, availability, ease of use, and environmentally friendly nature. These materials exhibit high efficiency in removing pollutants like dyes, heavy metals, and organic contaminants from wastewater. However, despite their widespread use, they also possess several limitations, including difficult recovery from aqueous solutions, poor selectivity toward certain dyes, low reusability, and a tendency to aggregate in water. These drawbacks hinder their broader application in practical wastewater treatment processes. To overcome these challenges, the integration of these materials into polymer or biopolymer matrices has emerged as a promising strategy. Polymers provide structural support, enhance dispersibility in aqueous media, and increase the reusability of adsorbent materials. This association not only prevents aggregation but also improves the selectivity and stability of the treatment materials in diverse wastewater environments. Among the most commonly researched polymers are chitosan [49], polyacrylamide [49,50], and polyvinyl alcohol (PVA) [51,52], which account for 23%, 11%, and 10% of studies, respectively. These polymers are chosen based on their solubility, biocompatibility, and the variety of functional groups they possess, which play a crucial role in the adsorption of pollutants. Chitosan, for instance, is widely used due to its solubility in acidic solutions (low pH), its biocompatibility as a natural biopolymer, and the presence of reactive amino and hydroxyl groups. These functional groups allow chitosan to form hydrogen bonds or electrostatic interactions with a wide range of contaminants, enhancing its adsorption capacity.

The diversity of functional groups found in polymers such as hydroxyl, carboxylic, amine, aromatic, aliphatic, and amide

groups further contributes to their effectiveness in wastewater depollution. For instance, carboxylic and amine groups can bind to heavy metal ions through ion exchange mechanisms, while hydroxyl and amide groups can form hydrogen bonds with organic pollutants like dyes. Polymers such as polyacrylamide and PVA, with their versatile chemical structures, are ideal for forming composite materials with enhanced adsorption properties [53]. These composites not only increase the adsorption surface area but also improve the interaction between the adsorbent and the pollutants, resulting in higher removal efficiencies. In addition to their adsorption capacity, polymers offer the advantage of tunable properties. By functionalizing polymer matrices with specific chemical groups, it is possible to tailor their selectivity toward targeted pollutants. This makes polymer-based materials particularly effective in addressing a broad spectrum of contaminants, ranging from organic dyes to inorganic heavy metals. Moreover, the reusability of polymer-based composites is significantly improved due to their structural stability and resistance to chemical degradation, allowing for multiple cycles of wastewater treatment with minimal loss of efficiency. Overall, the incorporation of polymers into wastewater treatment materials addresses the limitations of traditional adsorbents, offering a more robust, selective, and sustainable solution for water purification.

Due of their hydrophilic character and the covalent connections that form between their interlayers, clays are not suited for reacting or dispersing with most polymer matrices [54, 55]. Moreover, the clay layer stacks are tightly held together by electrostatic forces. To address this difficulty, modified clay particles are first distributed in polymer matrices. In essence, surfactant intercalation increases the spacing between the clay layered silicate sheets throughout the modification process. By making such modifications, it is possible to give clay minerals a hydrophobic quality that will enable the modified clay to disperse extremely finely in polymer matrices. There are two main methods for altering the structure of clay: (i) physical modification and (ii) chemical modification. The physical modification procedure involves only the adsorption of modifying chemicals on the surface of the clay. Although the clay particles are not altered by this method, the resultant polymer composites do benefit slightly from it. Be-

cause clay and the modifying chemicals have weak van der Waals forces, there may be a modest change in properties. On the other hand, the stacked silicates and the modifier initiate chemical reactions with the help of chemical modification. Moreover, the molecules are altered during the ion exchange process by the addition of cationic or anionic functional groups. Consequently, the clay's capacity to disperse in the polymer matrix is enhanced. The increased surface area and higher aspect ratio of clay particles when dispersed in polymeric composites, along with the nano-thick layers present in the clay material, are responsible for the enhanced mechanical, thermal, optical, and barrier properties of polymer/nano-clay composite systems [56,57].

Fabrication of Polymer/Clay Composites

Generally, the direct use of clays as a material for removing organic dyes is limited due to many inconvenient factors such as smaller surface area, low adsorption tendency to organic species, difficulty in recovering clay particles from aqueous solutions, and their reduction after regeneration. In order to overcome these limitations, researchers have developed clay-polymer nanocomposites [58,59]. Clays have a large field of application due to their attractive properties. A small amount of these substances can change the overall physical, chemical, and mechanical properties of polymers. Materials of type conventional composites or nanocomposites can be fabricated relying on the nature of the constituents, the treatment condition, and the resistance of the interface interactions between the polymer and clay layer surfaces. For the fabrication of conventional composites, the clay particles with their original aggregated state block the diffusion of the polymer between the interlayer spaces of the clay. These conventional composites generate properties similar to those of micro-composites with an advantageous improvement in modulus, consequently resulting in a lack of other properties such as resistance or toughness. If the clay is intercalated and exfoliated, the layers of the latter retain the multilayered structure of polymer and clay alternating in intercalated nanocomposites, whereas in exfoliated nanocomposites, the clay layers are well separated and randomly distributed in the continuous polymer matrix [60,61].

In order to improve the chemical, physical, and mechanical properties, various approaches are available for the polymer/clay nanocomposite synthesis, namely solution-blending, melt-blending, and in situ polymerization [62,63]. As a result, the nanocomposite involves uniform dispersion of clay, abundant functional groups, good compatibility, and thermal stability. Concerning the solution-blending procedure, the polymer is dissolved in a suitable solvent with the dispersing of the clay in the same solvent if possible or a different one in the aim to obtain a miscible mixture. The polymer solution is then intercalated or incorporated between the clay dispersion. In situ polymerization targets swollen clay layer sheets using a monomer solution where polymerization starts and propagates [64,65]. The polymerization initiating agent can be heat or a suitable chemical. This increase in the molecular weight between layers increases the basal spacing d_{001} , sometimes resulting in an almost fully exfoliated morphology. In order to obtain a thorough dispersion of clay, the melt-blending process is used. Clay is simultaneously incorporated into the annealed polymer matrix in a melt mixing device, and the resulting composite is kneaded to obtain an even distribution [66,67]. Organic modification by using polymer can create active functional groups and reform the surface charge on clays, raising the ability to eliminate the organics pollutants [68-70].

To investigate the potential of PVA-TrGO nanocomposites for biomedical applications, the antibacterial activity of the PVA-TrGO-1.5 wt % sample was studied. This sample was chosen because it exhibited the best thermal and mechanical properties among all samples. Pathogenic bacterial strains of Gram-negative *E. coli* (ATCC® 25922™) were used to evaluate the antibacterial activity by calculating the CFUs. Figure 1a-c shows the viability loss of the bacteria after 3 h of incubation with pure PVA, pure TrGO, and PVA-TrGO-1.5 wt %. Quantitative analysis based on CFUs, as illustrated in Figure 1d, indicated significantly reduced bacterial activity in the case of PVA-TrGO nanocomposites, showing an impressive ~3.5 log, which represents more than 96% reduction of *E. coli* viability, while the pure PVA matrix exhibited negligible antibacterial properties. The high antibacterial activity of the nanocomposites can be attributed to either of the following explanations: (a) direct contact of the bacteria with the edges of TrGO, which were able to pierce the cellular membrane, or (b)

wrapping of TrGO around the bacteria thanks to its two-dimensional structure, which prevented nutrient uptake by the bacteria, resulting in cell death [54,55]. The relatively lower antibacterial activity of pure TrGO flakes with respect to the PVA-TrGO nanocomposite can be attributed to its strong tendency for aggregation due to the presence of strong van der Waals interactions between the nanosheets [56]. This res-

tacking tendency of TrGO nanosheets causes the loss of its two-dimensional properties, leading to lower antibacterial activity with respect to homogeneously dispersed TrGO in a PVA matrix [57]. These results suggest that the PVA-TrGO nanocomposites, with superior mechanical and antibacterial properties, have the potential to become important materials in several biomedical applications.

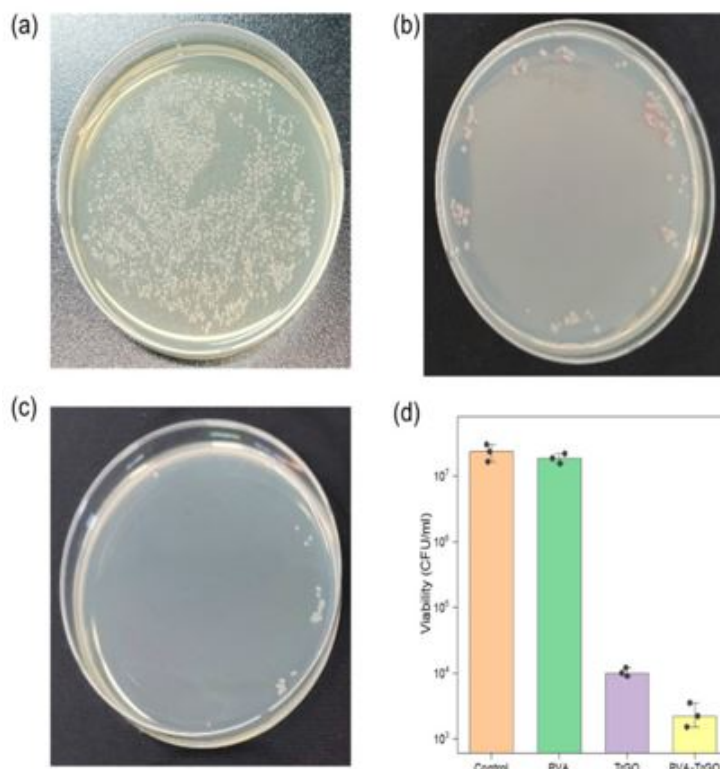


Figure 1: Antibacterial activity expressed as colony-forming units (CFU)/ml of (a) the pure PVA polymer matrix, (b) pure TrGO, and (c) PVA-TrGO 1.5wt % nanocomposite toward *Escherichia coli* (ATCC® 25922™) and (d) number of *E. coli* viable bacteria, calculated from CFU. Three independent measurements were performed for statistical analysis.

Characterization of Polymer/Clay Composites

Polymer/clay nanocomposites can be characterized by different methods depending on the desired applications. For example, analysis through zeta potential measurements is frequently used when employing polymer/clay nanocomposites in adsorption or catalysis fields. The surface properties change depending on the nature of the polymer used (a polymer with basic or acidic sites), as it allows the determination of the zero-charge point. Additionally, pH significantly influences zeta potential; at low pH, the surface may become positively

charged, favoring the adsorption of anionic dyes, while at high pH, the surface becomes negatively charged, enhancing cationic dye adsorption [69]. Then, all the modifications of these nanocomposites by functional organic group can be studied by FTIR analysis [70].

But the analyses most used to confirm the nature of the nanocomposites (intercalated, exfoliated, or immiscible) are XRD and TEM, often combining TGA thermal analysis to confirm their stability. The structural properties of nanocomposites have been widely studied using XRD analysis, from which the

different forms of nanocomposites can be determined. Regarding the immiscible form, in general, no shift of the characteristic peak of clay will occur. This is sometimes due to the size of the polymer and also related to its structure, in which the immobilization of a linear polymer in the galleries of the clay is better compared to the branched form [71]. Then, it is sometimes even difficult to immobilize the polymer in the galleries of the clay, which implies the use of other procedures. Among the most used procedures is the immobilization of surfactants with different carbon chains, which leads to the swelling of the interlayer distance. This is followed by an ion exchange process between the metal cations existing in the structure of the clay and the surfactants. Then, another method involves the use of ultrasonic radiation with a solu-

tion containing clay or organophilic clay and the polymer.

According to XRD analysis it was found that this method generates the formation of exfoliated or intercalated nanocomposites with a good dispersion of polymer in the clay galleries (**Figure 2**). From this figure, it is clear that the nature of the surfactant, its concentration, and the method used during the preparation significantly influence the structural properties of the obtained nanocomposites. Intercalation results an expansion of 2–3.5 nm of clay sheets, and they remain parallel to each other. Extensive penetration of polymer chains into the interlayer spaces of clay results in exfoliation of the clay sheets [71,72]. They are separated/dispersed during exfoliation by more than 10 nm.

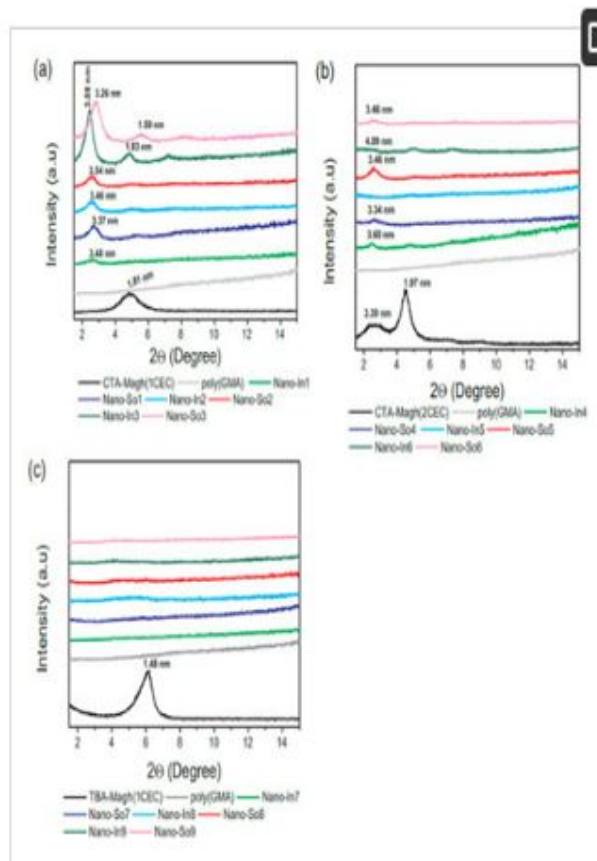


Figure 2: XRD patterns of nanocomposites obtained by different organoclays. (a) XRD patterns of nanocomposite prepared by an in situ method in organophilic clay galleries using ultrasound radiation (symbolized by So). CTA-Magh (2CEC) a clay modified by CTA⁺ surfactant using 1CEC. (b) XRD patterns of poly (GMA)/organophilic clay nanocomposite (containing 2CEC of CTA⁺). (c) XRD patterns of poly (GMA)/organophilic clay nanocomposite (containing 1CEC of TBA⁺).

Among the best techniques that can be combined with XRD analysis is TEM analysis. From **Figure 3**, the TEM images of Nano-So4 and Nano-So7 nanocomposites are totally different due to several modifications conducted for each sample. Nano-So4 nanocomposite is a material based on poly(GMA) and CTA-Magh (2CEC), while Nano-So7 contains poly(GMA) and TBA-Magh (1CEC); the TEM images of Nano-So4 show very fine lines with similar shapes corresponding to the intercalated form, while Nano-So7 nanocomposite shows non-uniform scattered lines corresponding to the exfoliated

form, which is in agreement with the XRD analysis [70]. So, for TGA analysis, this technique allows us to know the different stages of degradation as well as the hydrophilic/hydrophobic character and the stability of the nanocomposite. As it is known, the loss of mass of physisorbed water is generally observed at temperatures below 150 °C; at this stage, it is easier to determine the character of the resulting material. So, to establish whether the stability of the nanocomposite has been improved, it is very important to test the parent polymer without any modification.

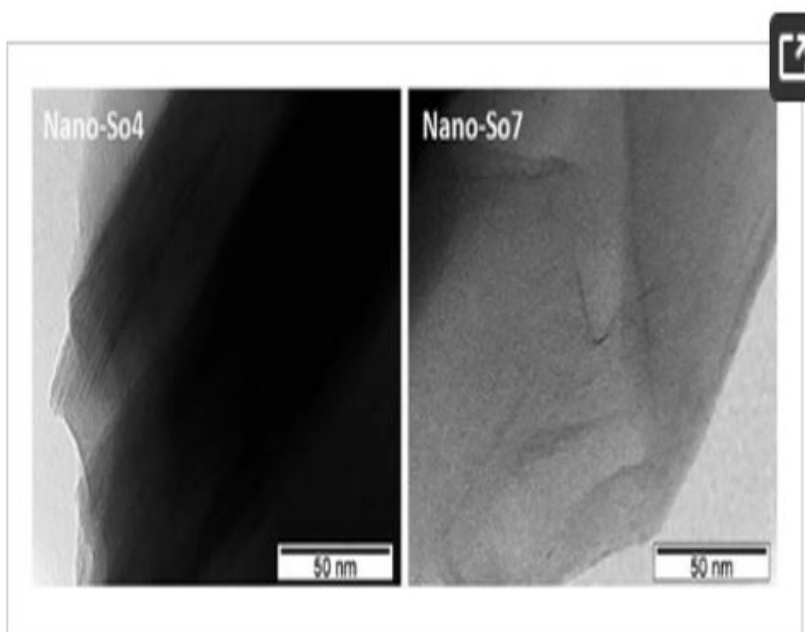


Figure 3: TEM images of nanocomposites Nano-SO4 and Nano-SO7

With nanocomposite prepared from an organophilic clay and cellulose acetate, there was a significant change in the degradation of the nanocomposite, from which it was confirmed that the nanocomposite has a greater thermal stability compared to the parent polymer, [71,72]. To achieve this stability, there is an optimal content of clay that should not be exceeded. It is clear that the CA/Mag 5% nanocomposite was the most stable material in this whole series of materials [72].

Dye removals

These colored substances are groups of atoms called chromophores whose light absorption causes color. A soluble dye is referred to as a dye; otherwise, it is a pigment [73]. In sever-

al application techniques, such as pharmaceuticals or food, a colorant can contain a combination of soluble molecules and insoluble particles. In biology, we speak of pigments for the molecules which naturally give color to the organisms that we study, and of dyes for the products that we add to the preparations to be studied. There are three types of colorings: natural ones, synthetic colors produced by the chemical industry but which exist identically in nature, and artificial colors, i.e., produced by the art of man and which have no equivalent in nature [74]. Synthetic dyes, commonly used in textiles, cosmetics, and the food industry, often find their way into wastewater, causing serious environmental pollution. These compounds are non-biodegradable and persist in aquatic systems,

leading to toxic effects on aquatic organisms and potential bioaccumulation. For example, dyes like crystal violet and methylene blue are harmful to fish and other aquatic species, while some, such as rhodamine and Congo red, exhibit carcinogenic and mutagenic effects in humans [75-79]. Addressing these harmful impacts is a critical focus of dye removal studies.

Polymer-based materials are organic compounds possessing a large specific surface area, micro porosity, and a three-dimensional network [80-85]. This gives them an advantage of use as adsorbents such as ion exchange resins, membranes, molecularly imprinted polymers, microporous organic polymers, etc., while their elaboration with other polymers or metals, clays, and zeolites for the formation of novel polymeric composite materials is important in the environmental field [85,86]. The tendency to develop low-cost adsorbents with high removal capacity has always been the focus of researchers for dye removal. Among the most powerful additives are clays, activated alumina, metal oxides, and zeolites. The advantages of clays are numerous compared to other additives; clays are cheap, abundant, have a porous surface, a high exchange capacity, and are respectful of nature. Their modification by certain inorganic or organic agents can overcome some disadvantages. Their layered structure allows penetration of polymer chains or in situ polymerization, and this results in equal or better performance in dye adsorption. These modifications made it possible to improve the surface of the composite with structural characteristics, also offering the opportunity for abundant functional groups [82-87]. The resulting composite exhibiting a variety of complex elimination mechanisms towards different types of dye O, H, S, N, and F groups. Elimination is achieved either via electrostatic attraction, surface hydrophobicity, π - π interaction, or hydrogen bonding. Over the years, this type of composite (polymer/clay) based on the inorganic (clay) and organic (polymer) substances has always been necessary, and it is very interesting to apply it as an adsorbent for wastewater treatment due to its compatibility, low cost, and lower toxicity.

Polymer/Clay-Composite-Based Catalysts

The utilization of metallic species as nanoparticles or oxides in the degradation or the reduction of various colorant-contaminated wastewaters is a very promising, simple, rapid, and efficient treatment method. These species as catalysts have unique electrical, optical, and thermal properties that are ideal, as well as having a high surface area and easy fabrication of their selectivity and specificity. Using the noble metals (Ag, Au, Pt, and Pd) for catalytic reduction is very common and widely investigated for wastewater depollution (Figure 4). The application of these species alone is unsuitable due to their agglomeration/aggregation along with the reduction in their performance and the difficulty of their reuse in aqueous solutions [88-94]. In order to minimize the inconveniences, several researchers used low-cost, abundant, and eco-friendly materials in the aim to immobilize/disperse these metals on their surface. Clays possess a high specific surface area and sheet-like structure with surface negative charges, which make them a suitable challenger as support for the immobilization/dispersion of metallic species using a simple method such as ion exchange. By using a chemical, biological, or thermal treatment, the nanoparticle species can be formed on the surface of the clay (Figure 5). To obtain an effective nanocomposite catalyst, polymerization or in situ polymerization can also increase other factors such as specific surface area and surface adsorption efficiency, minimize leaching of metals, and facilitate their use and reuse in aqueous solution. To limit environmental pollution, effective and environmentally friendly treatment strategies have been developed. Among these strategies is the application of advanced oxidation processes. These are oxidative treatment processes which require the presence of metallic catalytic support. After the diffusion of the pollutant in the nanocomposite surface, the metallic nanoparticles supported on the nanocomposite (polymer/clay) facilitate the dye reduction/degradation reaction. The catalytic reductions require the presence of a reducing agent such as NaBH_4 , NaOH , or LiBH_4 , whereas the photocatalytic reaction requires the presence of UV irradiation. In addition to using clay-based nanocomposites, these elimination pollutant techniques are preferable to other techniques due to their shorter elimination time, less toxic product, and their interesting reduction products as raw molecules, as well as their low cost, ease of design, and ease of process.

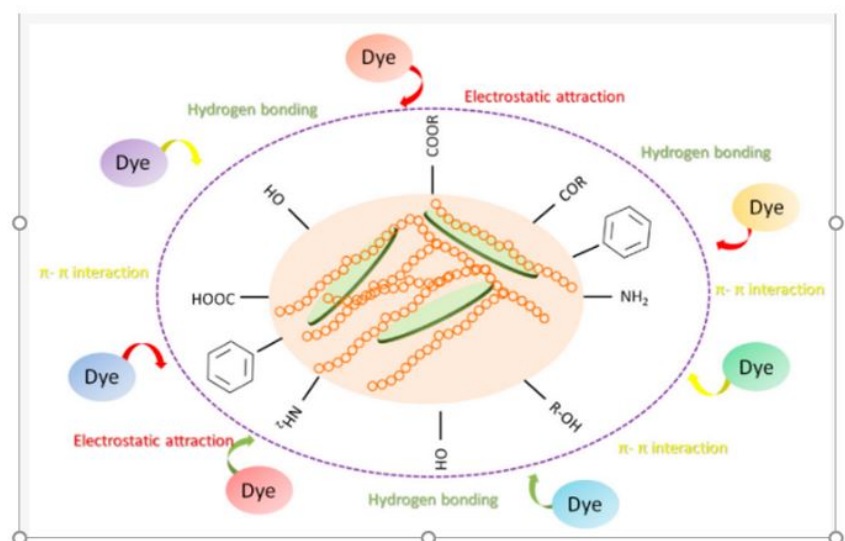


Figure 4: Mechanisms of dye removals

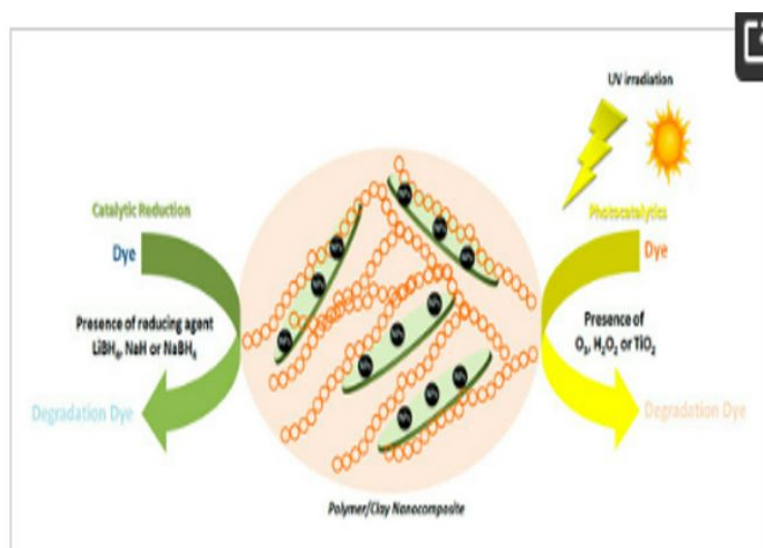


Figure 5: Dye removal with redox reactions

Dental Nanocomposites

Peri-implantitis affected parts become covered by an infected smear layer of instrumentation debris after routine implant preparation, which seems to compromise fibrin clot adhesion to such altered surfaces. In addition, continuous flap mobility and early clot retraction could draw the clot-blended graft complex away from the implant surface with subsequent creation of a micro-gap graft, epithelialization, and eventual implant surface recontamination. For that reason, treating a per-

i-implantitis affected implant surface should include complete removal of the infected biofilm and the smear-like layer, resulting in complete exposure of the roughened titanium implant surface. This should be followed by maximizing clot-blended graft adhesion to the implant surface through application of a graft material with a particle size smaller than that of the implant surface pores. Such mechanical integration is considered to reduce the possibility of the implant bone micro-gap, a factor that could ensure complete protection of the underlying defect-filled regenerative materials or blood clot.

This, along with subsequent enhanced bone regeneration, could be interpreted as a true re-osseointegration. Particle size seemed to be an important factor that optimizes adhesion of particles to the exposed implant surface. Such improved adhesion is likely to retard the apical migration of the epithelial attachment, a factor that could enhance reosseointegration. Further peri-implantitis affected surface conditioning with citric acid improves nanoparticle-sized hydroxyapatite-blended clot adhesion to titanium implant surfaces [95].

95. Ay Gamal, Abdel-Ghaffar KA, Iacono VJ (2013) A novel approach for enhanced nano particle sized bone substitute adhesion to chemically treated periimplantitis-affected implant surfaces: an invitro proof-of-principle study. *J Periodontol* 84(2):239–247

Particle size seemed to be an important factor that optimizes adhesion of particles to the exposed implant surface. Such improved adhesion is likely to retard the apical migration of the epithelial attachment, a factor that could enhance reosseointegration. Further peri-implantitis affected surface conditioning with citric acid improves nanoparticle-sized hydroxyapatite-blended clot adhesion to titanium implant surfaces (Gamal et al. 2013 [95]). Growth factors such as platelet-derived growth factor (PDGF) have significantly enhanced periodontal therapy outcomes with a high degree of variability, mostly due to the lack of continual supply for a required period of time. One method to overcome this barrier is gene therapy. Platelet-derived growth factor, PDGF-B gene delivery in fibroblasts using nanosized calcium phosphate particles (NCaP-P) as vectors, has found to significantly enhance fibroblast proliferation.

Nanomaterials for Periodontal Tissue Engineering Tissue engineering is an evolving interdisciplinary field integrating biology, engineering, materials science, and medicine that focuses on the development of biological substitutes to restore, replace, maintain, or enhance tissue and organ function. Tissue engineering concepts for periodontal regeneration are focused on the utilization of synthetic scaffolds for cell delivery purposes [96]. Although the employment of such systems offers promise, it is very likely that the next generation of materials will rely heavily on nanotechnology and its potential to

produce non-biologic self-assembling systems for tissue engineering purposes [97]. As detailed above, self-assembling systems for biologic systems are those which automatically undergo prespecified assemblies much in line with known biologic systems associated with cells and tissues. Using these principles, it is possible to construct systems on a nano-, micro- or even macroscale. Nanotechnology has got the potential to produce non-biologic self-assembling systems for tissue engineering purposes. It is possible to create polymer scaffolds in the future for cell seeding, growth factor delivery and tissue engineering via nanodevices implanted to sites of tissue damage. As native tissues or organs are composed of proteins within nanoscale and cells directly interact with nanostructured extracellular matrices (ECM), nanobiomaterials such as nanofibers, nanotubes, nanoparticles, and other nanofabricated devices with smaller than 100 nm in at least one dimension are able to contribute cell growth and tissue regeneration. Recent advances in nanotechnology, however, have enabled the design and fabrication of biomimetic microenvironment at the nanoscale, providing an analog to native ECM. Presently, materials available for such constructs are metals, ceramics, polymers, and even composite materials, the like of which have not yet been developed. The clinical utility of these nano-constructed self-assembling materials is their capacity to be developed into nanodomains or nanophases, leading to unique nanobuilding blocks with inbuilt nanocontrol and nanodelivery capabilities. Our present capacity to create polymer scaffolds for cell seeding, growth factor delivery and tissue engineering purposes is well recognized. In the future, these processes may well be manipulated via nanodevices implanted to sites of tissue damage. Example that defines the benefits of nanotopographic patterning is the addition of chemically etched, nanoscale roughness to the surface of porous polylactic-co-glycolic acid, PLGA scaffolds—a method that has been shown to enhance cell adhesion and growth, as well as the expression of matrix components [98].

Need of Nanotechnology in dentistry

Nanotechnology is a science that works at the molecular level. It deals with structures ranging in the size of 100 nm or smaller in at least one dimension and developing materials or devices within that size [99]. Nanotechnology deals with the

nanostructures, nanomaterials, nanoparticles, etc. Simply, this technology gives manipulation of matter on molecular and atomic levels to bring out enormous changes in applications of various fields. One such important field is dentistry [100]. As you go down with the size of particles, the physical and chemical properties change that can be useful to apply in different fields. Dentistry is one such field where nanotechnology plays various roles such as tissue engineering [101], nanodental implant [102], dental nanorobots [103], nanocomposites [104], dental nanostructures [105], nanomaterials for periodontal drug delivery [106], dental imaging [107], nanomedicines such as toothpastes etc. [108]. In recent years, the increasing interest in aesthetic restoration has led to further development of materials that have the same color as that of teeth. Nanotechnology allows the production of nano-sized filler particles that are compatible with dental

composites; therefore, a greater amount of filler can be added into the composite resin matrix [109]. Composite resins containing such particles are easy to shape and have a high degree of strength and resistance to abrasion. Restorative dentistry comes up with the modern advancement where aesthetic filing comes into picture. These filling materials are nothing but the resin matrix with nanofillers mixed evenly into it. Nanofiller plays an important role in enhancing the properties of dental restorative filling materials in many ways, like its physical, mechanical, biological properties, its appearance. Nanofillers due to its smaller size, larger surface area, and high surface energy make it convenient to capture reactive monomer or polymer segment on its surface [110]. They also favored stressing transfer from soft resin matrix to hard organic nanofiller. Thus, resin-based composite materials have acquired nanotechnology for future progress and upcoming years will elaborate the topic further for more advancement.

Nano in Composite Resins

No synthetic nanocomposite material is better enough to be ideal for dental applications. Thus, in an attempt to improve the applicability of these nanocomposite materials, they have undergone progressive evolution from bulk-filled dental composites [111] to nanofiller dental composites [112]. The development in the use of nanocomposites patented in response to

the persistent and discouraging issues of polymerization shrinkage, strength, microhardness, and wear resistance essential in posterior occlusal applications. Around in the same era where Bowen developed the resins specially for restorative dentistry [113], a new word 'nano' was introduced by the scientist Nobel Laureate Sir Richard Feynman in 1959. This discovery was a landmark for advances in dental composites and nanoparticles as fillers. Choice of nanoparticles is based on their physical properties, tackle issues like polymerization shrinkage, wear resistance, microhardness, and achieve patient satisfaction in terms of the aesthetic appearance [114]. Despite many improvements in this field, dental composites do not have enough toughness, strength, and durability in order to be used in stress-bearing areas. A variety of nanofillers was chosen to figure out their effects on final products such as nanoparticles of silica, glass, carbon nanotubes, alumina, zirconia, titania.

Nano-silica as Fillers

Crystalline quartz or silica is the first kind of fillers that were used in resin nanocomposite materials. Natural silica is nonreinforcing and has been used as a filler, only to reduce the cost. Silica and glass fillers are used in a wide range of dental applications because of its biocompatibility, wear resistance, and aesthetics. They are, however, subject to brittle failure [115]. The positive effect of nanosized silica and 74 R. Silicate-based fillers on flexural strength, surface hardness, fracture toughness, and optical properties has already been reported in the literature [116].

Carbon Nanotubes

Fillers Carbon nanotubes are used in the preparation of composite materials that are biocompatible in nature and give high mechanical strength and resilience [117]. But these materials showed lack of hydrophobicity and chemical inertness that limits their applications.

Nano-zinc as Fillers

Zinc oxide is naturally white in color, and its incorporation into this new dental amalgam might fade the metallic color of the conventional amalgam out. Specialty of zinc oxides is

their antibacterial properties [118]. ZnO probably has the richest family of nanostructures of all materials, both in structures and in properties. Its percentage loading is high which increases the mechanical properties of the resin [119]. This affects the polish ability of the final composite and thus finally its look.

Nano-alumina as Fillers

Nano- and micro-sized alumina nanoparticles were used for improving the mechanical properties of the materials. The effect of alumina addition and reported a positive impact on the properties of acrylic resin. It was chosen due to their unique properties like high elastic modulus, thermal and chemical stability, high strength, toughness. Comparing the two, nanosized filler was proved to be more effective [120].

Zirconia as Fillers

A lot of work has been already done with zirconia as fillers in composite materials. In addition to that, zirconia-silica nanofibres were used [121] in the past few years. Zirconia is biocompatible, chemically inert, corrosion resistant, opaque in nature, low thermal conductivity, etc. They need to be present in higher amount as fillers ~60–70% in content which is responsible for the toughness, whereas research is now in focus on minimum amount of filler content, i.e., less than 10%.

Nanohydroxyapatite as Fillers

Hydroxyapatite (HA) is a natural mineral containing calcium and phosphate. It is very much suitable for dental applications as it is biologically compatible and substituent for dentin [122]. It gives excellent bioactivity, enhances physical strength, and is the most stable form of calcium phosphate. More work has been done on nanohydroxyapatite and glass ionomer cement for restoration [123]. It resulted in an increased resistance to demineralization and acceptable bonding strength. Nanophase crystals of HA can bind to the bone and stimulate bone healing by the stimulation of osteoblastic activity [124]. However, the setting time of nano-HA cement

exceeded the clinically suitable maximum setting time.

Nano-TiO₂ as Fillers

Titanium dioxide (TiO₂) nanoparticles, for example, are very fine, agglomerate easily in practical applications, and are especially difficult to disperse in organic solvents [125]. But it shows excellent properties if synthesized in a controlled manner. Adding surface-modified TiO₂ nanoparticles improves the microhardness and flexural strength of dental resin-based composites [126]. Though the researchers have not yet achieved the level of increasing mechanical strength with reduction in polymerization shrinkage, it is mainly due to the size and type of nanoparticles they have used.

Current Progress

Increasing demand for aesthetic dentistry has led to the development of resin composite materials for direct restorations with improved physical and mechanical properties, aesthetics, and durability. It seems that no single material is better enough to satisfy all its desired properties of dental composites. It is required to have a kind of material which gives high mechanical strength, good aesthetic properties, etc. To come up with this conclusion, fillers should have good chemical and physical properties, optimum size distribution of smaller and larger particles, etc. Nanohybrid is the mixture of smaller and larger particles where smaller particles reside in between the gaps of larger particles and larger particles take care of the consistency of the paste and provide wear resistance. Smaller particle size also helps in reducing the polymerization shrinkage. Other factors are color (shade), translucency, fluorescence, and opalescence (optical properties) that give natural tooth its vital-looking appearance [127]. The rest of the impressive features of TiO₂ nanoparticles are that they are nontoxic and have high refractive index and antibacterial properties, white in color, chemically inactive, corrosion resistance, high microhardness, etc. Furthermore, the literature has also shown that nanoscale TiO₂ reinforcement agents bring new optical, electrical, physiochemical properties attained at very low TiO₂ content, 76 R. Table 1 exhibits the physical and mechanical properties of nanocomposite resins.

Characteristics	Macrofilled	Microfilled	Microhybrid	Nanohybrid
Size (μm)	8–12	0.04–0.4	0.4–1.0	0.5–3
Inorganic filler (wt%)	60–70	35–67	75–80	80–90
Compressive strength (MPa)	250–300	250–350	300–350	350–400
Tensile strength (MPa)	50–65	30–50	40–50	75–90
Elastic modulus (GPa)	8–15	3–6	11–15	15–20
Curing shrinkage (vol.%)	–	2–3	2–3	2–3
Water sorption (mg/cm^2)	0.5–0.7	1.4–1.7	0.5–0.7	0.5–0.6

Table 1: Comparison of physical and mechanical properties of nanocomposite resins of various filler sizes

Polymer–TiO₂ nanocomposites as a promising new class of material it will be commercially beneficial for widespread fields [128]. The major concern is synthesis of nanohybrid TiO₂ particles and its high cost. Green synthesis together with microwave-assisted nanoparticles synthesis can be a protocol to overcome this problem. Recently, green synthesis using fruit peel extract, an agricultural waste, and rapid microwave synthesis with respect to size and shape of nanostructures were generated [129]. This may help in reducing the cost for TiO₂ nanoparticles by keeping the quality unaltered by using microwave technique. Fruit peel contains phytochemicals that act synergistically as capping agent in biosynthesis of nanoparticles in hybrid form. Agricultural waste reduces the cost of process, hazardous chemical waste, etc., and microwave synthesis reduces the time from several hours to few minutes. Dentistry and green chemistry both are the most important and promising fields. This protocol will be the best example of green chemistry and dentistry that will move forward with hand in hand. Major importance goes to the final physical and mechanical properties of the material. It is seen that the properties of nanohybrid materials are superior to macrofilled, microfilled, macrohybrid, microhybrid, etc. Thus, TiO₂ nanohybrid synthesized by green and microwave method would be an appropriate solution.

Properties of Nanoparticles in Orthodontics

The characteristic of nanoparticles like the size, shape, and surface characteristics determine the properties of the nanoparticles. Nanoparticles have properties different from micro-particles due to their small size and relatively large surface area. When the size of a particle is close to or smaller than the

de Broglie wavelength of the charge carrier (electrons and holes) or the wavelength of light, the periodic boundary conditions of the crystalline particle are destroyed, or the atomic density on the amorphous particle surface is changed [130]. Due to these, a lot of the physical properties of nanoparticles are quite different from bulk materials, yielding a wide variety of new applications. Optical properties of nanoparticles are due to the excitation of surface plasmons in metallic nanoparticles, this property can be used in biomedicine, energy, and environment protection technologies [131]. Magnetic properties of nanoparticles are by virtue of its external magnetic field and hence can be used for biomedical imaging and information storage technology. The adhesion and the friction of nanoparticles play important roles in nanofabrication, lubrication, the design of micro/nano devices, colloidal stabilization, and drug delivery. Controlling the size, shape, and surrounding media of metal nanoparticles are important as many of their intrinsic properties are determined by these parameters. Particular emphasis has recently been placed on the control of shape, because, in many cases it allows properties to be fine-tuned with a greater versatility that gives the particles a unique nature. It is only within the past decade that it has become possible to control the shape of particles synthesized in solution, and numerous methods have been developed for this. Stabilizing agent also plays a role in the size of nanoparticle. The key effect of the stabilizer on the nanoparticle size lies in the initial particle nucleation stage [132]. A thermodynamically stable and mature nanoparticle can only be formed when a nucleus grows into a cluster that is larger than a certain critical size. Therefore, a fast-initial nucleation is critical to the production of stable nuclei and subsequently smaller nanoparticles. The higher the temperature, larger and more

polydisperse nanoparticles are obtained. Similarly, change in pH or H⁺ activity can impact the reduction of ions. As the reduction of H⁺ proceeds, the solution pH goes up, which favors the reduction of metal ions.

Nanotechnology and Nanobiomaterials in Dentistry

New potential treatment opportunities in dentistry may include different approaches: (a) Building up particles by combining atomic elements: i.e., bottom-up approach. This is applied in local anesthetics, hypersensitivity cure, dentifrices, orthodontic treatment, diagnosis and treatment of oral cancer. (b) Using equipment to create mechanically nanoscale objects: i.e., top-down approach [133]. Examples include nanocomposites, impression materials, nanosolutions, nanoneedles, nanotweezers, and bone replacement materials. (c) In addition to bottom-up and top-down approaches, there is the functional approach. This approach disregards the method of production of a NP; the objective is to produce a NP with a specific functionality [134]. Nanotechnology has been applied to many specialties in the dental field. For instance, effective drug delivery systems were generated for the treatment of periodontal diseases. NPs impregnated with antimicrobial agents were produced in order to maintain therapeutic concentration of the agent in the periodontal pocket for a sufficient length of time to ensure eradication of the bacteria present [135]. Moreover, toothpastes containing nanosized calcium carbonate enabled remineralization of early enamel lesions as a prophylactic measure to prevent dental caries [136]. In the same context, NPs of amorphous calcium phosphate (CaPO₄) dental composite restorative materials were developed and were described as “smart” because they release calcium and phosphate ions at a cariogenic pH [8] and remineralize tooth lesions [137].

Nanotechnology in Endodontics

Almost every aspect in endodontics has gained advantage of the newly emerging nanotechnology. Different types of nanoparticles used in endodontics and other applications.

Radiography

By using dental digital radiographies obtained with nanophos-

phor scintillators, the radiation dose is diminished and high-quality images are obtained [138].

Local Anesthesia

To induce oral anesthesia in the era of nanodentistry, a colloidal suspension containing millions of active analgesic micron-sized dental NPs is instilled on patient's gingivae. After contacting the surface crown or mucosa, ambulating nanorobots reach the pulp. Once installed there, analgesic dental NPs may be commanded by dentist to shut down all sensitivity in any particular tooth that requires treatment [139].

Dentin Hypersensitivity

Dentin hypersensitivity is defined as sharp pain arising from exposed dentin as a result of various stimuli such as heat, cold, chemical, or osmotic and that cannot be ascribed to any other pathology. Occlusion of the exposed and patent dentinal tubules is an effective method to provide relief from dental pain [140]. Nanoparticles of carbonated apatite, silica, bio-glass, and functionalized hydroxyapatite have been used for the management of dentin hypersensitivity [141]. They occlude the dentinal tubules within minutes offering patients a quick and permanent cure [141]. The main advantage of using nanoparticles is their size, which allows them to be pushed deeper into dentinal tubules. Furthermore, these nanoparticles, once modified, could promote remineralization of the demineralized dentin [142].

Endodontic Filling Materials

Different types of nanoparticles were investigated for their antimicrobial potential against endodontic pathogens: A. Silver Nanoparticles (Ag NPs) The antimicrobial properties of Ag NPs have been generally exploited in nanofiber materials, bandages, wound dressings, and ointments. Ag NPs also prevented bacterial colonization on various surfaces such as catheters, prostheses, and clothing [143]. Mechanism of action: Silver (Ag) works in a number of ways to disrupt critical functions in a microorganism. It attacks multiple sites within the cell to inactivate critical physiological functions such as cell wall synthesis, membrane transport, nucleic acids (DNA and

RNA) synthesis, protein folding and with transport [144]. The mode of action of Ag NPs has been proposed to be identical to one of the Ag ions. The positively charged Ag NPs interact strongly with the cell membrane modifying its permeability [145]. Moreover, the Ag NPs interact with multiple targets in the microbial cell, such as enzymes and plasmids, providing the bacteria least capacity to gain resistance [146]

Ag NPs with size in the range of 10–100 nm showed powerful bactericidal potential against gram-positive and gram-negative bacteria. A root canal irrigating solution of 0.1% Ag NPs imparted limited antibacterial effect against *Enterococcus faecalis* biofilm, while an intracanal medicament of 0.2% Ag NPs gel applied for 7 days led to the destruction of *E. faecalis* biofilm and the number of viable bacterial cells was significantly decreased [147]. Further, a mixture of calcium hydroxide [Ca(OH)₂] and Ag NPs had a potential advantage in eliminating *E. faecalis* from root canals [148].

Advanced Nanomaterials and Their Functionalization

The surface charge on Ag NPs was important in bactericidal efficacy against *E. faecalis*. When NPs with positive, negative, or neutral surface charges were compared; the positively charged Ag NPs were effective against *E. faecalis* and exhibited a high level of cytocompatibility [135]. Ag NPs dispersion was found to be biocompatible, especially in lower concentrations [136]. Chitosan Nanoparticles (CS NPs) Chitosan is a polysaccharide derived from chitin, one of the most abundant natural polymers in the biosphere. Chitin is the main component of the exoskeleton of marine crustaceans (e.g., shrimps, crabs). It is currently receiving a great deal of interest for medical, pharmaceutical, and agricultural applications because of its biodegradability, biocompatibility, nontoxicity, and antiviral properties [149]. It can be synthesized in various forms such as powder, capsules, films, scaffolds, hydrogels, and beads [149]

Nanoparticles of calcium hydroxide (CaOH NPs) itself were prepared and were compared to chitosan NPs as intracanal medicaments for 1 week and 1 month. The highest depth of penetration into dentinal tubules was recorded by the CaOH

NPs, while the greatest fracture resistance was found with the CS NPs.

Zinc Oxide NPs (ZnO NPs)

ZnO NPs and a mixture of ZnO/CS NPs produced a significant reduction in the number of *E. faecalis* adhering to dentin [137] and were able to disrupt the multilayered biofilm architecture [138].

The antibacterial activity of the polycationic ZnO NPs was attributed to the electrostatic attraction with the negatively charged bacterial cell, which might lead to the altered cell wall permeability, resulting in leakage of the proteinaceous and other intracellular components and death of the cell [139]. ZnO nanocrystals were biocompatible and allowed new bone formation and remodeling [140].

Bioactive Glass (BG) Bioactive glass received considerable interest in root canal disinfection due to its antibacterial properties. Mechanism of action: The antibacterial mechanism of BG has been attributed to several factors acting together: the high pH due to release of ions in aqueous environments [150], the increase in osmotic pressure more than 1%, which is inhibitory for many bacteria, and the induced mineralization on the bacterial surface due to calcium/phosphorus precipitation [150]. However, it was less effective than calcium hydroxide in preventing residual bacterial growth [151]; it was also less effective in eliminating biofilms compared to the planktonic counterparts [150–152].

Photodynamic therapy (PDT)/photosensitizers

The recent advances toward achieving predictable endodontic disinfection focused on newer alternatives such as PDT. PDT is based on the injection, ingestion, or topical application of a photosensitizer dyes followed by visible light activation [153]. There are two classical PDT mechanisms: production of radical ions of oxygen (type I) or singlet oxygen (type II) [133]. Mechanism of action: PDT uses a specific wavelength of light to activate a nontoxic dye (photosensitizer), leading to the formation of ROS and singlet oxygen. These reactive oxygen or singlet oxygen molecules are highly reactive and damage bacterial cell wall, membrane lipids and proteins, and nucleic

acids, which eventually promote bacterial cell death [153]. This antibacterial mechanism confers PDT with the advantage of broad-spectrum antibacterial activity and a lower risk of developing resistance. However, a reduction in the uptake of the photosensitizers into the bacterial cells could be one of the clinical factors compromising the antibacterial effect of PDT [123]. Moreover, the antibacterial activity of PDT was compromised in the presence of root canal constituents such as pulpal tissue, serum, dentin matrix, and bacterial remnants [135].

Photosensitizers

Phenothiazines and xanthenes are two classes of photosensitizers commonly tested for antibacterial efficacy [154]. B. Rose bengal (RB) is an anionic xanthene dye. It is water soluble, nontoxic and absorbs light in the visible spectral region [155]. However, its application is strongly limited by the fact that it tends to aggregate in aqueous solutions.

Dentin Stabilization

Collagen is the main structural protein of human dentin [140] and contributes to its viscoelasticity, ultrastructural stability, and tensile strength [141]. Degradation of collagen by bacterial enzymes can facilitate microbial penetration, compromise structural integrity, and lower the resistance of dentin to fracture [124]. Moreover, matrix metalloproteinases (MMP-1, MMP-2, MMP-8, and MMP-9) are found in dentin collagen matrix and play an important role in its physiological and pathological degradation [142]. Activation of these MMPs can occur by some root canal irrigants during endodontic treatment. Among the materials tested to inhibit the action of these MMPs were chitosan and its derivatives, due to its ability to neutralize MMPs [142]. PDT enhances cross-linking of collagen fibrils in the dentin matrix, thereby increases the tensile strength and elastic modulus of collagen, and improves dentin stability [123]. It is a rapid process in which the proteins and collagen molecules are covalently cross-linked when illuminated in the presence of appropriate photosensitizers [143]. However, the cross-linked collagen may become stiff and brittle. Thus, the incorporation of polymeric fillers would reinforce the collagen structure and serve as spacers in between the collagen fibrils [143, 144]. One promising

method of improving collagen cross-linking and reducing degradation is the use of PDT in combination with polycationic chitosan nanoparticles. Chitosan nanoparticles (CS NPs) and PDT inhibit the activity of bacterial collagenases. Thus, combining PDT and binding to CS NPs inhibit bacterial-mediated collagenolytic activity and enhance the mechanical properties of collagen matrix [134].

Endodontic Filling Materials

Root canal obturation is one of the essential steps for successful endodontic treatment aiming at preventing the reinfection of root canals that have been chemomechanically cleaned, shaped, and disinfected. Adequate root canal obturation is achieved through entirely filling the root canal system and providing a tight seal. Three-dimensional root canal obturation requires the use of a core material (gutta-percha, resilon, or coated cones) and root canal sealer.

Obturing Core Material

Gutta-percha has always been and remains the most widely used root canal obturating material. It presented a slight antibacterial activity due to its zinc oxide component [145]. However, studies have shown that endodontic microorganisms have high affinity for gutta-percha [146,147]. This could lead to persistence of infection in the root canals. Therefore, antimicrobial agents were integrated into gutta-percha points to improve their antibacterial properties. Calcium hydroxide gutta-percha points (Roeko GmbH +Co., Langenau, Baden-Württemberg, Germany), Active Point (chlorhexidine containing gutta-percha), MGP (iodoform containing gutta-percha) (Medidenta), and TGP (tetracycline containing gutta-percha) (Medidenta) could be given as examples for commercially available preparations. On the other hand, gutta-percha was coated with nanosilver particles in an attempt to enhance its antibacterial effect [148]. This new material has displayed significant antibacterial and antifungal properties against *E. faecalis*, *Staphylococcus aureus*, *Candida albicans*, and *Escherichia coli* [148]. Moreover, nanosilver-coated gutta-percha was cytotoxic to mouse fibroblasts after 1 hour and decreased with time to become similar to standard gutta-percha after 24 h and 1 week [149].

Root Canal Sealers

One of the desired properties of root canal sealers is their antimicrobial properties. The common sealers possess antibacterial activity for a maximum period of 1 week, with most of them showing a significant reduction in antibacterial properties immediately after it sets [156, 153]. With recent advances in material science and nanotechnology, nanoparticles were incorporated into novel root canal sealers to improve their physical, chemical, biological, and antibacterial properties. They highly interact with microbial cells due to their higher surface area and charge density. Types of nanoparticles added to root canal sealers: The development and characterization of root canal sealers were performed with nanoparticles of quaternary ammonium polyethyleneimine nanoparticles (QPEI NPs), zinc oxide nanoparticles (ZnO NPs), chitosan nanoparticles (CS NPs), calcium phosphate nanoparticles (CP NPs), and bioactive glass nanoparticles (BG NPs). A. Antibacterial Properties Incorporation of cationic nanoparticles such as CS NPs and ZnO NPs in zinc oxide based and resin-based root canal sealers improved their antibacterial effect [154,155]. It was added CS NPs in the epoxy resin-based and calcium silicate-based root canal sealers and found that this addition enhanced the antibacterial activity of epoxy resin-based sealer whereas no extra benefit was shown in calcium silicate-based sealer. Epoxy resin-based and polymer-based sealers with added QPEI NPs eliminated the growth of *E. faecalis* for 4 weeks [156-158]. The incorporation of QPEI NPs did not change the antimicrobial activities of ZnO-based and resin-based endodontic sealers in fresh state, while addition of QPEI NPs resulted in great increase in the antibacterial effect of ZnO-based sealer after aging for 7 days.

Biological Properties of polymers

Biocompatibility

The biocompatibility of nano-ZnO sealer was comparable to unmodified ZnO-based sealer and less cytotoxic to murine fibroblasts than epoxy resin-based sealer [159]. In an animal study, nano-ZnO sealer induced similar tissue reaction to epoxy resinbased and commercial zinc oxide and eugenol-based sealer. It exhibited satisfactory biocompatibility on subcutaneous tissue of rats after 15, 30, and 60 days of implanta-

tion [160]. Additionally, nano-ZnO sealer was more biocompatible with human gingival fibroblasts than commercial micro-sized ZnO- and resin-based sealers [161]. Abramovitz et al. showed that the addition of QPEI NPs to epoxy resin-based, polymer-based, and methacrylate resin-based sealers did not impair their biocompatibility, since QPEI NPs did not leach into surrounding tissues [162].

Bioactivity

An experimental bioactive methacrylate endodontic sealer containing amorphous calcium phosphate nanoparticles (CP NPs) was developed. It aimed at helping the remineralization of root dentin and thus strengthening the roots [162]. This bioactive sealer released calcium and phosphate ions for a long period of time and has been proposed as a promising root canal filling material. Merspublications investigated the physical properties of nanomodified sealers. Addition of CS NPs did not alter the flow characteristics of ZnO-based root canal sealer [154]. Incorporation of QPEI NPs increased the setting time, hydrophilicity, wettability, and surface charge of ZnO-based and epoxy resin-based sealers [159]. Loading with nano-zirconium oxide particles as radio pacifier enabled the penetration of portland-based and epoxy resin-based sealers in dentinal tubules at the apical third, thus improving their retention and sealing ability [163]. It was observed that replacing conventional ZnO powder in Grossman sealer with ZnO NPs decreased the setting time and dimensional changes of the sealer [164]. Moreover, loading with 25% ZnONP improved the physicochemical properties such as setting time, flow solubility, dimensional stability, and radiopacity of Grossman sealer [165]. Addition of nanohydroxyapatite to methacrylate-based root canal sealers caused no alteration in their radiopacity and film thickness [166].

Commercial Sealers Produced with Nanotechnology

Guttaflow is a silicon polymer-based root canal sealer that is composed of finely ground gutta-percha, poly-dimethylsiloxane and nanosilver. Nanosilver is biocompatible, prevents the spread of bacteria, and does not cause corrosion or color changes in the sealer [69]. Nanoceramic Sealer (NCS) (B&L Biotech, Fairfax, VA, USA) is another calcium silicate-based sealer that has been compared with other commercial calci-

um silicate-based sealers and was found to support periodontal ligament stem cell survival [167].

Nanobiomaterials in Endodontics

Biomaterials are materials that stay in close contact with vital tissues such as pulp, periradicular tissues, or periodontal ligament for extended periods of time. They have an extensive usage in the field of endodontics including pulp capping, pulpotomy, perforation repair, root-end filling, apexogenesis, and apexification procedures. The majority of endodontic biomaterials are mainly composed of calcium hydroxide or calcium silicate. Nanotechnology application in endodontic biomaterials emerges in two ways. One of them is nanomodification of the content of the material, and the other way is to add nanoparticles into the composition of the material. Both nanomodification and incorporation of nanoparticles are expected to provide better biological and physicochemical properties.

Vital Pulp Therapy

Vital pulp therapy is aiming at treating pulp injuries by capping the pulp, to stimulate the formation of tertiary dentin and maintain pulp vitality. Nanosized bioactive glass (BG) particles possess a higher specific surface area, a more regular size, and better bioactivity compared with traditional BG particles [168]. Nanocrystalline hydroxyapatite (HA) paste was found biocompatible and superior to formocresol when tested as pulpotomy and pulp capping agent [160]. It was also recommended as a substitute for MTA and Dycal in direct pulp capping [169]. Moreover, incorporation of 3%wt. nano-hydroxyapatite increased the compressive strength of calcium hydroxide cement and enhanced the release of calcium ions which indicates mineralization capacity that is desired for inducing hard tissue formation in pulp capping procedures [170].

Endodontic Surgery

Root-End Filling Materials

Chogle et al. found that the addition of NPs to the monomer matrix of root-end filling materials reduced apical leakage significantly [80]. The cytotoxicity of a polymer nanocomposite resin was not significantly different from that of ProRoot

MTA and Geristore [150].

Mineral Trioxide Aggregate (MTA)

Mineral trioxide aggregate (MTA), introduced into the endodontic literature in 1993 [169], has been widely preferred by clinicians due to its biocompatibility, bioactivity, and good sealing ability [170]. However, MTA has some shortcomings like long setting time, weak handling characteristics, and discoloration potential [163]. It was found that the addition of nanosilica to MTA accelerated the hydration process, reduced the setting time, and had no adverse effect on its compressive and flexural strengths. Moreover, the addition of Ag NPs to MTA improved its antimicrobial efficacy [171] and induced similar inflammatory reaction.

Nanowhite mineral trioxide aggregate (Nano-WMTA) produced via reducing the size of particles of WMTA and adding tricalcium aluminate, calcium sulfate, zeolite, and strontium into the composition exhibited decreased setting time [88], low surface porosity, and more resistance to acidic environment than WMTA [174]. Furthermore, the greater surface area of nano-WMTA and incorporation of nano-tricalcium aluminate induced faster release of calcium ions and significantly raised the calcium content, as well as the pH of the environment compared to conventional WMTA. This displayed favorable histopathological reactions and contributed to bone regeneration in the mandible of rabbits [156]. These nanobiomaterials resemble bone neutral minerals in size and composition promoting desirable osteoconductive activity [143]. In fact, nano-WMTA has been proposed in the situation of periapical inflammation [158]. 52 H. M. Abou El Nasr and M. B. Akbulut Zirconium oxide (ZrO) nanoparticles were added into the composition of white portland cement as radiopacifier. This ZrO blended cement revealed accelerated hydration process and decreased solubility. Besides, incorporation of ZrO nanoparticles did not cause alteration in antimicrobial activity against *S. aureus* and *E. coli*, but exhibited slightly more antibacterial activity against *Pseudomonas aeruginosa* [163].

Dental Composite Materials

The composites typically involve organic phase, i.e., matrix, inorganic phase, i.e., fillers and coupling phase (coupling

agent) that binds the organic and inorganic entities together. Apart from matrix and inorganic phase, composite materials

need photo initiator to initiate polymerization [4]. Thus, dental composite materials was tabulated in Table 2.

Types of composites	Filler
Densified [7]	<60% by volume
– Midway filled	Particles <3 μm
Ultrafine	Particles >3 μm
Fine	>60% by volume
– Compact-filled [8]	Particles <3 μm
Ultrafine	Particles >3 μm
Fine	
Microfine [9]	Average particle size = 04 μm
– Homogeneous and heterogeneous	
Industrial use	Blends of densified and microfine composites [10]
Traditional	Equivalent to what are termed macrofill composites in other classifications
Fiber-reinforced [11]	Industrial-use composites

Table 2: Dental Composite materials

Dental Resin Matrix

Resin is a main matrix and is chosen in such a way that it has the ability to polymerize. There are different polymerizing reactions that can initiate polymerization in the presence of light, heat, cold conditions and/or in the presence of catalyst, etc. Polymerization depends upon the type of resin material. Polymerization is a chemical reaction that transforms small molecules into large polymer chains [172]. The polymerization of composite materials is never complete. The large percentage of reactive groups does not participate in polymerization. In addition, any surface layer exposed to air is incompletely polymerized. Polymerization shrinkage occurs when the dental composite is cured and changes the properties of the resin by chemical reaction, such as condensation, polymerization, or addition. Resin systems shrink during polymerization mainly because the monomer molecules are located at van der Waals distances (4 angstrom) from one another, while the corresponding polymers are within a covalent bond distance (1.5 angstrom) to each other. This accounts for the shrinkage during the polymerization process [173]. As the light-curing resin materials are very much convenient to use, they are in use on regular basis extensively. The resin monomer matrix should possess C=C group in their structures that can polymerize in the presence of photoinitiation to give a rigid polymer. Methacrylate polymeric networks with good resistance to aqueous milieu are sought for use in both prophylactic and restorative dentistry [174].

Advantageous of Dental Biomaterials

Biomaterialization is the process of minerals deposition within or outside of the cells [153]. Dental materials capable of bonding to the tooth's tissues and inducing repair are called the biomaterials. Bioactivity is defined as the material's ability to adhere to the living tissue [154]. After placement, the chemical interaction between the biomaterial's surface and the tissue's compounds takes place—this process is called a “bioactive fixation” [159]. Biomaterials in dentistry include bioceramics divided into a large area of other subjects, e.g., glass ceramics, silica-based glass (popularly called the bio-glass), zirconia, alumina, titania [155]. Generally, they are described as bioactive, biocompatible, and resorbable. The bio-glass, which is the most widely used biomaterial, can form FHA crystals, thus inducing biomineralization. Moreover, this process proved to be thermodynamically stable at the physiological pH, which, in case of pulpal cells irritation caused by caries, may be decisive upon their survival. The ratio of calcium to phosphorus in bioglass is stable in body fluids, which decides on its prolonged bioactivity and resistance to being chemically interfered [155].

Nanoparticles in Impression Materials

Physical properties of polyvinylsiloxane impression materials were improved by the addition of nanosized silica. The study was carried out in which six types of fillers including nano-

sized fumed silica were added to polyvinylsiloxane impression materials. They had reported that the fumed silica was effective in increasing the viscosity, tensile strength, and maximum % strain. Irreversible hydrocolloid, i.e., alginate impression powders can be mixed with water that contains silver hydrosol nanoparticles to make an alginate impression. This will reduce microbial cross-contamination by bacteria, yeasts, fungi, and viruses to the stone model from the infected impression [143]. Nanofillers are added to vinyl poly siloxanes, thus producing novel addition silicone impression materials. This material is claimed to have better properties such as flow and improved hydrophilic properties that helps in avoiding voids in the impression and model as well [144]. It was evaluated the antimicrobial activity and properties of two commercially available irreversible hydrocolloid impression materials (Zelgan and Tropicalgin) after incorporating varying concen-

trations of AgNPs (**Table 3**). They concluded that adding silver nanoparticles to irreversible hydrocolloid impression materials alginate resulted in superior antimicrobial activity without having any adverse effect on their properties. Addition of silver nanoparticles to Zelgan alginate impression material significantly increased the gel strength compared with the control group. An increase in the permanent deformation was found with the incorporation of AgNPs of both Zelgan and Tropicalgin. The flow of Zelgan increased with the incorporation of AgNPs, whereas a decrease in the flow of Tropicalgin was observed at 1 and 2 wt% of AgNPs. An increase in the gelation time of both Zelgan and Tropicalgin was observed with the incorporation of AgNPs. They concluded that AgNPs can be incorporated into irreversible hydrocolloid impression materials as antimicrobial agents without adversely affecting their properties [145].

Dental materials	PMMA	Ceramics ZrO ₂ Al ₂ O ₃ glass ceramic	Metal Ti ₆ Al ₄ V CoCrMo CoCr
Advantage	Good biocompatibility, esthetics processability, and reparability	High strength, suitable color, and low thermal and electrical conductivity	Titanium alloy has high strength, low density, light weight, low shrinkage, nonmagnetic, good mechanical properties and corrosion resistance, and nonallergic, teratogenic, and carcinogenic. CoCr alloy has high strength, wear resistance, and less tooth tissue cutting, with good biological safety. CoCrMo has good corrosion resistance, wear resistance, ductility, gloss, anti-plaque adhesion, and biosafety
Disadvantage	Poor strength, low fracture resistance, radiopacity behavior, and microbial adhesion	Low ductility and brittleness	Further improvement is desired to improve the corrosion resistance and biocompatibility of the Ti and CoCrMo alloy. CoCr alloy easily leads to sensitive symptoms
Nanoresearch	TiO ₂ nanoparticle reinforced the mechanical behavior of PMMA. Well-dispersed nano-ZrO ₂ particles can improve the modulus and strength and maintain or even improve ductility. Ag TiO ₂ and Fe ₂ O ₃ particles significantly reduce adherence of <i>C. albicans</i> of PMMA and do not affect metabolism or proliferation	The hardness and fracture toughness increased nanozirconia ceramics. Glass ceramics with nanosized grains showed excellent corrosion resistance, high fracture toughness, and translucency	Nanophase metals (specifically, Ti, Ti ₆ Al ₄ V, and CoCrMo alloys) promote osteoblast adhesion, proliferation, differentiation, and mineralization

Table 3: Properties of prosthodontics materials

Silver Nanoparticles in Maxillofacial Prosthesis

Maxillofacial prostheses are used to restore lost facial parts.

Candida albicans infection remains a problem for maxillofacial prostheses made of silicone, as the microorganism causes degradation of the material and infection of the tissue. Fungal infection as a result of *Candida* adherence on the surface of the material is always a problem for maxillofacial patients [152]. The intaglio or anatomical surface of maxillofacial prostheses is exposed salivary and nasal secretions. That is why these prostheses are susceptible to biofilm formation and colonization by microorganisms, with subsequent degradation of the prosthesis [153]. The coating of silicone materials with AgNPs could be of great use to prevent fungal infection for patients with maxillofacial prostheses. It was studied biocompatibility and antifungal properties of silicone facial prostheses coated with silver nanoparticles (AgNPs). Medical-grade silicone disks were coated with 5 and 50 mg/ L 21 dispersions of either AgNPs or AgNO₃. They showed that silicone prosthetic materials coated with AgNPs are biocompatible with fibroblast cells and showed antifungal properties. This study demonstrated that AgNPs-coated silicone elastomer had antifungal activity without appreciable adverse effects on human dermal fibroblast cells [154].

Silver Nanoparticles in Dental Implants

Titanium has been used for dental implants due to their good biocompatibility, better mechanical strength, and great corrosion resistance [155]. Failures in dental implants are due to lack of stability or misfit at the implant abutment interface [156]. Micro-gap on the interface of two-piece implants with variable fluid flow at this interface leads to the bacterial infiltration and inflammatory cells that leads to the bone loss around this area. Some failures are due to the infection and inflammation [157–159]. Surface modification of titanium-based implant is done to avoid implant failure. Due to the interaction of the implant surface with bone and gingival and also, partial exposition of implant to the oral cavity that includes bacteria, fabricating a coating material with both antimicrobial activity and biocompatibility is important and leads to implant success [160]. Nanoparticles have also been used as coatings to the implant surface to improve osseointegration. Coating of bioinert nanomaterials like zirconium and aluminum over titanium implant surfaces may change the physical properties and enhance the osteogenic potential of

implants [161]. It has been also reported that materials such as titanium nanotubes are able to increase the density of osteoblast cells on the implant that may lead to better implant stability [162]. Al₂O₃ nanoparticles help in osseointegration and in the healing process around dental implant. It helps in new bone formation with haversian canals, osteoblast, and osteocyte and also improves mechanical properties of dental implants [163, 164]. Silver nanoparticles coating helps to prevent the growth of bacteria and thus helps in osseointegration. Titanium is a biocompatible material widely used in medical and dental implants. After implantation, titanium surfaces are prone to bacterial colonization that could lead to bacterial infection, inflammation, and finally lead to implant failure. Silver nanoparticles (AgNPs) are known as antibacterial agents, and their integration to titanium surfaces decreases the risk of implant failure.

Advantages of Using Nanotechnology in Dentistry

Mechanical properties of dental materials deeply affect their clinical success. Dental materials should have adequate strength to withstand the static and dynamic occlusal forces for a long period of time in the complex environment of the stomatognathic system. What makes the concept of nanomaterials interesting is that their size is smaller than the critical lengths defining many physical events. The major advantage of using nanobiomaterials in dental practice is their improved mechanical properties, superior abrasion resistance, lower shrinkage, and enhanced optical and esthetic properties [180].

These non-agglomerated and discrete nanoparticle preparations can be homogeneously distributed in dental resins and coatings to create composite materials for dental applications [169]. More effort has been put forth to improve the physical properties of composite materials that suffer from problems like polymerization shrinkage, weak coatings, triage risk, microhardness, and meager aesthetic satisfaction [178]. Nanocomposites are primarily used as dental materials with improved anti-decay potential. Dental surgeons prefer nanocomposites over conventional composite materials as they provide long-lasting tooth structural properties in patients [150,166,170]. The most widely used nanofillers in nanocom-

posites include aluminosilicate powder-based nanocomposites, which exhibit advanced physicochemical properties such as superior hardness, excellent flexure, best color density and polishing-retention ability, strength, improved modulus of elasticity, super translucency and good aesthetic appeal, and reduced filling shrinkage [178,179]. Dental nanocomposites are also used in restorative dentistry to mimic the properties of natural enamel. They add volume to composite resin and fillers, exhibit high strength and ion-releasing properties, prevent tooth decay, and restore fractures [171,172]. Moreover, they have a potential application as mineral provisions as they release fluoride phosphate and calcium when applied in increasing nano-positing formulations such as nanodicalcium phosphate anhydrous (DCPA)-whiskers or tetra calcium phosphate (TTCP)-whiskers, and polymer-kaolinite nanocomposites [180]. The aesthetic application is pronounced for nanocomposites because of the reduced shrinkage and polymerization characteristics that increase filler volume and decrease resin matrix [173,174]. Moreover, they prevent tooth decay with increased fluorapatite and well-informed mechanical resistance. The nanocomposites also have

high strength and ion-releasing properties which make them effective in preventing caries and restoring fractures [173,175]. The enrichment properties of nanocomposites directly facilitate remineralization and the mechanical strength benefits more from the additional amounts of nanofillers up to certain limitations [76]. There are some cases reported in which nanocomposite denture materials employ the use of inorganic fillers at the nanoscale, which are outstanding for their color retention, durability, and high abrasion resistance properties in comparison to the acrylic or microfiber compositions [177]. Examples of nanocomposites used in dentistry include Filtek Supreme, which contains glass particles and amorphous calcium phosphate (NACP) [146,177].

Classification of Nanoparticles in Dental Materials

Nanomaterials are differentiated by size and structural composition, which in turn dictates their physiochemical properties. Some of the major nanomaterials are briefly discussed below in table format. Table 4 shows the nanotube-based nanomaterials that are currently being explored for dental applications [170-182].

Nanomaterials	Properties	Benefits and Applications	References
Nanoparticles	<ul style="list-style-type: none"> Conventional or unconventional. 	<ul style="list-style-type: none"> Easily manufactured; Flexible in application. 	[30-32]
Metallic nanoparticles	<ul style="list-style-type: none"> Antibacterial characteristics. 	<ul style="list-style-type: none"> Infections treatment. 	[33,34]
Silver nanoparticles (AgNPs)	<ul style="list-style-type: none"> Antibacterial, antiviral, and antifungal properties; Induce microorganisms cell death; Prevent secondary caries; Easy combination with bioactive substances; Strengthen dental composites; Flexural strength and elastic modulus; Improve dental health; Biocompatible; Long-lasting antibacterial activity. 	<ul style="list-style-type: none"> Restorative materials; Dental fillers; Dental aesthetics; Endodontic sealers; Remineralization; Dental restorative materials; Dental implants, dental prostheses. 	[34-37]
Carbon nanotubes	<ul style="list-style-type: none"> Increased surface area; Active substance delivery to cells; Quick attachment to the tooth and cementum surface. 	<ul style="list-style-type: none"> Tooth fillers; Tooth coatings. 	[38-40]

Nanomaterials	Properties	Benefits and Applications	References
Aluminum oxide nanoparticles (Al ₂ O ₃ NPs)	<ul style="list-style-type: none"> • Sensitive to sunlight, heat, and moisture; • Polished surface wear resistance; • Hardness, good biocompatibility; • Improved mechanical strength; • Improved mechanical and thermal properties; • Reduced water absorption and solubility; • Reduced friction. 	<ul style="list-style-type: none"> • Aesthetics applications. 	[1,50,53]
Silicon dioxide nanoparticles (SiO ₂ NPs)	<ul style="list-style-type: none"> • Improved mechanical qualities; • Low toxicity; • Good biocompatibility. 	<ul style="list-style-type: none"> • Fillers; • Dental restorative materials; • Polishing agents; • Medicinal compounds. 	[1,16,54]
Zirconia	<ul style="list-style-type: none"> • Reduced bacterial adhesion; • Protection against caries; • Excellent polisher; • Comparable mechanical properties and color; • Low cytotoxicity; • Good biocompatibility and great fracture resistance. 	<ul style="list-style-type: none"> • Dental polishers; • Natural. 	[50,52]
Silica-based NPs	<ul style="list-style-type: none"> • Prevent dental caries; • Biocompatible; • Minimal toxic effect; • Low density; • High adsorption capacity; • Cost-effective; • Reduce tooth roughness. 	<ul style="list-style-type: none"> • Dental filling agents' dental hypersensitivity treatment; • Antibacterial agents and tooth polishing. 	[35,54]
Nanomaterials	Properties	Benefits and Applications	References
Graphene-based NPs	<ul style="list-style-type: none"> • Cost-effective; • Fracture-resistant; • Low-density; • Homogeneous crystal lattice structure; • Effective against bacterial biofilms. 	<ul style="list-style-type: none"> • Tooth coatings; • Tooth implantations; • Biofilm reduction. 	[41,42]
Gold nanoparticles (AuNPs)	<ul style="list-style-type: none"> • Inert; • Biocompatible; • Antibacterial properties; • Stimulate bone growth; • Preserve bone formation; • Chemical functionalization. 	<ul style="list-style-type: none"> • Nano-drug delivery systems; • Treating and detecting cancers; • Photothermal agents; • Contrast agents; • Nano-drug delivery carriers; • Osteo inductive agents; • Dental implants. 	[33,34,36]
Copper nanoparticles (CuNPs)	<ul style="list-style-type: none"> • Antimicrobial activities; • Prevent adhesive interface; • Maintain formulation properties. 	<ul style="list-style-type: none"> • Dental materials. 	[43]
Metal oxide nanoparticles	<ul style="list-style-type: none"> • More stable as compared to metal NPs; • Antibacterial properties. 	<ul style="list-style-type: none"> • Dental fillings. 	[33,44-46]

Zinc oxide nanoparticles (ZnO NPs)	<ul style="list-style-type: none"> • Antibacterial efficacy; • Less cytotoxic effects. 	<ul style="list-style-type: none"> • Dental composite resins; • Dental materials. 	[47-49]
Titanium dioxide nanoparticles (TiO ₂ NPs)	<ul style="list-style-type: none"> • High strength; • Corrosion resistance; • Excellent biocompatibility; • Antibacterial properties. 	<ul style="list-style-type: none"> • Titanium alloys; • Composite resins. 	[24,50,51]
Titania-based NPs	<ul style="list-style-type: none"> • Long-term effect on dental implants; • Decreased bacterial adherence; • Increased hardness. 	<ul style="list-style-type: none"> • Dental implants. 	[24,50,51]
Zirconium dioxide nanoparticles (ZrO ₂ NPs)	<ul style="list-style-type: none"> • Rigidity; • Improved radio-capacity; • Fatigue resistance; • Wear resistance; • Biocompatibility; • Osteo conductivity; • Decreased plaque buildup; • Strength; • Bending resistance; • Good appearance; • Improved fracture toughness; • Color stability. 	<ul style="list-style-type: none"> • Cosmetic applications; • Fillers. 	[50,52]
Nanomaterials	Properties	Benefits and Applications	References
Aluminum oxide nanoparticles (Al ₂ O ₃ NPs)	<ul style="list-style-type: none"> • Sensitive to sunlight, heat, and moisture; • Polished surface wear resistance; • Hardness, good biocompatibility; • Improved mechanical strength; • Improved mechanical and thermal properties; • Reduced water absorption and solubility; • Reduced friction. 	<ul style="list-style-type: none"> • Aesthetics applications. 	[1,50,53]
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Zirconia	<ul style="list-style-type: none"> • Reduced bacterial adhesion; • Protection against caries; • Excellent polisher; • Comparable mechanical properties and color; • Low cytotoxicity; • Good biocompatibility and great fracture resistance. 	<ul style="list-style-type: none"> • Dental polishers; • Natural. 	[50,52]
Silica-based NPs	<ul style="list-style-type: none"> • Prevent dental caries; • Biocompatible; • Minimal toxic effect; • Low density; • High adsorption capacity; • Cost-effective; • Reduce tooth roughness. 	<ul style="list-style-type: none"> • Dental filling agents' dental hypersensitivity treatment; • Antibacterial agents and tooth polishing. 	[36,54]

Table 4: Nanotube-based nanomaterials currently being explored for dental applications

Conclusion

The nanocomposite polymer matrices are highly efficient for their multidimensional perspective and application. Recently PNCs are applicable in different manufacturing industries for different propose like as dental restoration in medicine, automobile, drug-delivering, and in the food packing industry. Nanocomposite polymer matrices are very potential for future use, but there are still many improvements to bring. Generally, the optimization of physicochemical functions such as charging density, hydrophobicity, porosity, and mechanical and thermal stability of polymer nanocomposites is important. Also, the aggregation of nanofillers within the polymer matrix is a major issue to ensure the uniform distribution of nanofillers across polymer nanocomposites. Future research in the synthesis and application of polymer nanocomposites should focus on three key areas: reducing the carbon footprint, leveraging artificial intelligence (AI), and utilizing 3D printing. First, developing environmentally friendly synthesis methods that minimize energy consumption and reduce waste is crucial for decreasing the carbon footprint. Research should explore alternative, sustainable materials and processes that offer the same or better performance as traditional methods. Second, AI has the potential to revolutionize the design and optimization of polymer nanocomposites by providing predictive models for material behavior and guiding synthesis processes. This can lead to more efficient use of resources and shorter development cycles. Finally, 3D printing technology can significantly enhance the manufacturing of polymer nanocomposites by enabling precise control over material properties and structure, reducing material waste, and customizing applications to meet specific needs. By integrating these advancements, researchers can develop more sustainable, efficient, and innovative polymer nanocomposite solutions for a wide range of industries.

The ongoing development of polymer/clay composites for the removal or degradation of textile effluents continues to show great promise. The synergistic interactions between the organic polymer matrices and inorganic clay components generate

composites with a broad range of functionalities, offering significant selectivity towards various organic pollutants. However, considering the extensive diversity of dyes in textile wastewater, current polymer/clay composites can remove only a limited subset of organic dyes. This highlights the urgent need for the development of new, multifunctional composites that can effectively target a wider range of pollutants, including complex mixtures of dyes and other organic contaminants. One of the key challenges in advancing this field lies in the design of composites that can address a broader spectrum of pollutants while maintaining economic and practical viability for large-scale applications. Future research should focus on creating materials that not only have enhanced adsorption and catalytic properties but are also cost-effective, easily recoverable, and capable of maintaining high efficiency after multiple cycles of use. Despite the significant progress made in the application of polymer/clay composites for wastewater treatment, several limitations persist. These include difficulties in recovering the composites from aqueous solutions after use, the decline in adsorption efficiency after repeated cycles, low selectivity for certain types of dyes, and challenges in desorbing the adsorbed dyes from the composite matrix. Furthermore, the formation of by-products during dye degradation or reduction processes may introduce new concerns regarding secondary pollution. To overcome these challenges, it is crucial to adopt a multi-disciplinary approach that integrates experimental and theoretical methods. Additionally, the development of novel surface modification techniques and the incorporation of functional nanoparticles could significantly enhance the selectivity and reusability of these composites. In summary, while polymer/clay composites have demonstrated remarkable potential in wastewater treatment, especially in the removal of textile dyes, further advancements are required to address their current limitations. The future direction of this research should focus on the development of composites that are not only more versatile in pollutant removal but also environmentally sustainable, economically viable, and scalable for industrial applications. Continued efforts in both material innovation and theoretical understanding will be essential in achieving more effective and sustainable solutions for wastewater management.

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