

Polymer-reinforced hybrid composites: Review

Akram Kharir Saleh Edkheil *, Zaynab Aboulqasim Faraj Albireek **, HOUDA TAHIR IBRAHIM, Khaled Elgergeni ***

* Department of Dental Materials - lecturer at Department of dental technology of Medical sciences and Technology Collage (Tripoli) Libya.

** Department of Biomedical Engineering- Division of Biomechanics--- Head of Department of dental technology, and lecturer at Department of dental technology of Medical sciences and Technology Collage (Tripoli) Libya

*** BDS, MPHIL, PhD. Restorative dentistry --.... Director of scientific affairs of High Institute of Medical Science & Technology Tripoli.

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Abstract

Background: Polymer composites for use in prosthetics contain several components, but the main ingredients are the organic component-matrix and the inorganic component-reinforcement. The physical-mechanical properties of the composite depend on the reinforcement content, the bond between the matrix and the reinforcement as well as on the reinforcement distribution. Hybrid composite materials are a combination of either two types of matrix with one reinforcement or two types of reinforcement in one matrix, and other combinations are possible. In that way, it is possible to design and modify - cut the physical-mechanical and functional properties of composites, and process materials with predefined properties.

Within the framework of this final master thesis, the influence of the composition and structure as well as the process parameters of obtaining a hybrid composite material on the thermal and mechanical properties of the obtained composite will be analyzed. The correct choice of components and design of modern composite materials for use in prosthetics based on acrylate with reinforcement in the form of polymer fibers and particles will be considered.

The synergistic effect of different reinforcements as well as modifications of the reinforcement-matrix boundary surface will be monitored through the resulting mechanical properties-hardness and toughness. **Materials:** For polymer matrix mostly the commercial acrylic denture resins were used. Commercial acryl denture material "Simgal-Acryl R", Galenika AD, Belgrade, Serbia, was used as autopolymerized acrylic resin [47, 54]. It is a two-component system consisting of a powder and a liquid. The powder consists of a PMMA copolymer and the initiator benzoyl peroxide (BPO) in a concentration of 1.1% w/w. The liquid was made of methyl methacrylate (calc) 94.15% w/w; acid as methacrylic acid 19.8 ppm w/w; N, N-dimethyl-p-toluidine as accelerator 0.85% w/w; ethylene glycol dimethacrylate as cross-linking agent 5.00% w/w; water 27 ppm w/w. **Conclusion:** Organic-inorganic nanocomposites have wide application in dentistry and prosthetics.. Inorganic materials play a key role in sustaining and supplementing mechanical properties of polymer matrices and in further favoring cellular behaviors. As a result, in dentistry, biocompatible nanocomposites are able to be substituted for native tissue as shown in many clinical cases. **Keywords:** Polymer composites, component-matrix, Hybrid composite materials.

1. Introduction

Considering advantages of ceramics in dentistry and prosthetics which include biocompatibility and durability, esthetic appearance, such materials have some clear disadvantages. Brittle catastrophic fracture and abrasive wear of the natural teeth unless low fusing ceramics are used, are some of potential disadvantages [1-3]. Mechanical properties and fracture resistance of ceramic crowns depends on different factors, such as fabrication method, surface microstructure, finish of the crowns and the packing conditions before loading until fracture. Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Scientists and engineers realized early on that mixtures of materials can show superior properties compared with their pure counterparts. One of the most successful examples is the group of materials called composites, which are formed by the incorporation of a basic structural material into a second substance, the matrix. Usually the systems incorporated are in the form of particles, whiskers, fibers, lamellae, or a mesh. Most of the resulting materials show improved mechanical properties and are regularly used for lightweight materials with advanced mechanical properties,

usually are linked to the volume fraction, size and the shape of the filler particles.

Development of modern medicine also shifts focus to organic-inorganic systems that can bond to a tooth, show wear resistance, biocompatibility and satisfy esthetic standards. Composites have emerged as substitute for amalgams, due to their favorable physical and mechanical properties. Amalgams, despite some of their good properties have several disadvantages, but probably the biggest shortcoming is potential risk of mercury poisoning. Probably the most promising development in restorative dentistry is the associated procedure of attaching resin composites to hard tooth tissues. Over the last decade, substantial progress was achieved to improve the properties of dental resin composites in order to enable their usage in load bearing restorations. Composite resins are now being used in stress-bearing posterior restorations with increased frequency even though they were first used as anterior restorative materials. Resins were introduced in dentistry in late 1960s and since then they have endured a lot of changes in order to become restorative materials with satisfactory aesthetic and mechanical properties comparable to those of dental amalgam. Dental composites consist of a polymerizable resin matrix, usually urethane dimethacrylate (UDMA) or ethylene glycol dimethacrylate, glass particulate fillers, and a silane coupling agent. Polymerization of the resin matrix is either light activated or chemically initiated. The silane coupling coats the surface of the hydrophilic filler particles, allowing them to couple with the hydrophobic resin matrix. Research of the composite materials structure is mostly focused on the resin matrix monomers so as to improve properties like stress, biocompatibility, viscoelastic and thermal properties, polymerization shrinkage and filler content which plays a huge role in other properties, like reduce shrinkage, hardness, elastic modulus, flexural strength and compressive strength. Better mechanical and aesthetic properties promoted ongoing demand of direct restoratives for specific applications. Organic end of the molecule usually tends to bond with the resin matrix, merging in the process organic and nonorganic phase in the composite, whilst organic-nonorganic adhesive is usual addition to filler particles with nonorganic end of the molecule bonds. Usually new dental composites contain paste made with a mixture of cross-linked agents with silane treated glass of the filler (i.e. ceramic particles) with different sizes. In order to promote adhesion, silane as a coupling agent is used on different surfaces such as epoxy, polyester or methacrylate resins which are organic polymers or glass and ceramics which are minerals. Most of the dental composite materials that appeared in the past 15 years are some combination of silane-coated inorganic filler particles. Usually the filler particles are either barium silicate glass, quartz or zirconium silicate, often combined with very small-sized particles of colloidal silica.

for example in the construction of vehicles, sports equipment, devices, etc. In order to improve polymer composites mechanical properties fillers with smaller dimensions, in the micrometer range are added to the polymer. Those properties are

In order to predict their behavior in the oral environment, the investigation of the resin-based restorative materials elastic properties is very important. The elastic modulus quantifies the relative stiffness or rigidity of a material within the elastic range and may be described as the ratio of uniaxial stress to strain at small strain levels. The elastic parameters of a material are indicative of the deformation of the material under external forces. Elastic modulus is of great importance for the longevity of both the restoration and the surrounding dental tissue since dental restorative materials must withstand the masticatory

This Research paper investigates processing of different hybrid denture polymer composites with the aim to improve their mechanical properties. More than one type of fillers will be embedded to achieve improvement and the proper analyses will be conducted. Mechanical tests will show if the fillers are effective in building superior hybrid composite material.

2.Methodology

forces in the oral cavity. It is possible that the tooth structure will suffer from a fracture or that the bond between tooth and restoration will be compromised if the composite has a low modulus and in that case it will deform more under the functional stresses. If the composite has a low modulus, it will deform more under the functional stresses and it is possible that the tooth structure will suffer from a catastrophic fracture or that the bond between tooth and restoration will be compromised leading to marginal gap deformation, post-operative sensitivity and secondary caries. Also, the stresses at the post-gel phase of polymerization which are extremely important for the polymerization shrinkage and the strain are related to the elastic modulus of the composite. Incorporation of nanotechnology is one of the most recent advancements in the direct dental restorative materials. Nanotechnology is the engineering of functional systems at the molecular scale, understanding and control of matter at dimensions of roughly 1–100 nm. Both aesthetics and mechanical performance showed improvement in nanofilled composite resins - nanocomposites. Polymer nanocomposites (PNC) compared to more conventional composites have showed considerable mechanical improvements at lower fillers content, which in return makes processing of such composites simpler. Even though PNCs can be tracked back to 1950s they did not get substantial attention until synthesis of nylon 6-clay composite material which was reported by the Toyota research group. Considering remarkable enhancement of physical and mechanical properties with the addition of a small filler volume fraction compared to traditional composites, PNCs have attracted considerable interest in academia as well as in industry. Some of the improved mechanical properties can include yield stress, fracture toughness, ultimate stress, shock resistance and Young's modulus (or stiffness). In dental materials, improvements in high flexural strength, low polymerization shrinkage, low abrasion and resistance to fracture are especially important. Mechanical performance improvement of nanocomposites is due to the nanosize dimensions of the fillers (as a result of a very large aspect ratio), and to the durable filler - polymer interactions that can affect the effectiveness of load transfer between polymer matrix and the nanofillers.

Hybrid polymer composite materials show improved mechanical properties coming from a synergy of different reinforcements. Combinations used can be divided into groups: particles-fibers, particles-particles, particles-whiskers and fibers-fibers. The idea behind creation of hybrid material is that every reinforcement improves a different property. For example, certain particle filler can improve hardness, while chosen fibers increase toughness. This leads to a number of filler combinations that can produce superior materials in all industries. Dental materials can be modified to withstand higher impact force and to have excellent elastic properties and high biocompatibility at the same time.

In general, the reinforcement is supposed to be the strongest of all of the components, and therefore, in structural composites, its main role is to enhance the overall mechanical properties of the resulting material. The matrix is required to fulfill several functions, most of which are vital to the performance of the material. As a first approximation, it can be stated that the matrix holds the reinforcement in place to define the shape of the final product. The roles of the matrix in fibre-reinforced and particulate composites are quite different. The binder for a particulate aggregate simply serves to retain the composite mass in a solid form, but the matrix in a fibre composite performs a

2.1 THEORETICAL PART

2.1.1 Composite materials

Composite is a material made from two or more constituent materials with significantly different [physical](#) or [chemical properties](#) that, when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure, differentiating composites from [mixtures](#) and [solid solutions](#). The 'composite' concept is not a human invention. Wood is a natural composite material consisting of one species of polymer – cellulose fibres with good strength and stiffness – in a resinous matrix of another polymer, the polysaccharide lignin [4]. The idea of combining different materials in order to take advantage of the peculiar positive properties of each single constituent has ancient historical roots. However, it is only in the last half century that the science and technology of composite materials have developed sufficiently to provide engineers with a novel class of materials and the necessary tools to enable them to use them advantageously [4]. A structural composite is a material system consisting of two or more phases on a macroscopic scale, whose mechanical performance and properties are designed to be superior to those of the constituent materials acting independently [5]. In general, a composite consists of three components: the matrix as the continuous phase; (the reinforcements as the discontinuous or dispersed phase, including fibre and particles; and the fine interphase region, also known as the interface [6,7]. By carefully choosing the matrix, the reinforcement, and the manufacturing process that brings them together, the engineers can tailor the properties to meet specific requirements [8].

Composites are commonly classified at two distinct levels. The first level of classification is usually with respect to the matrix constituent. The major composite classes include

- 1) organic- matrix composites (OMCs),
- 2) metal- matrix composites (MMCs) and
- 3) ceramic- matrix composites (CMCs).

The term 'organic- matrix composite' is generally assumed to include two classes of composites:

- polymer- matrix composites (PMCs) and
- carbon- matrix composites (commonly referred to as carbon-carbon composites) [11].

The second level of classification refers to the form of the reinforcement:

- 1) particulate reinforcements,
- 2) whisker reinforcements,
- 3) continuous- fibre laminated composites and
- 4) woven composites [11].

[9]. What is more, modern composite materials are usually optimized (with respect to the aforementioned aspects) to achieve a particular balance of properties for a given range of applications [11]. However, as a common practical definition, the term 'composite materials' may be restricted to emphasize those materials that contain a continuous matrix constituent that binds together and provides form to an array of a stronger, stiffer reinforcement constituent. When designed properly, the new combined material exhibits better strength than would each individual material. The main advantages of composite materials

variety of other functions, which must be appreciated to understand the true composite action which determines the mechanical behavior of a reinforced material. These functions should therefore be considered in some detail [9]. The matrix binds the fibres together, holding them aligned in the important stressed directions. Loads applied to the composite are then transferred into the fibres, the principal load-bearing component, through the matrix, enabling the composite to withstand compression, flexural and shear forces as well as tensile loads. The ability of composites reinforced with short fibers to support loads of any kind is dependent on the presence of the matrix as the load transfer medium, and the efficiency of this load transfer is directly related to the quality of the fiber/matrix bond. The matrix must also isolate the fibres from each other so that they can act as separate entities. Many reinforcing fibres are brittle solids with highly variable strengths. When such materials are used in the form of fine fibres, not only are the fibres stronger than the monolithic form of the same solid, but there is also the additional benefit that the fibre aggregate does not fail catastrophically. The matrix should protect the reinforcing filaments from mechanical damage (abrasion) and from environmental attack. Through the quality of its 'grip' on the fibers (the interfacial bond strength), the matrix can also be an important means of increasing the toughness of the composite [9]. Composites have unique advantages over monolithic materials, such as high strength, high stiffness, long fatigue life, low density and adaptability to the intended function of the structure. Additional improvements can be realized in terms of corrosion [10]. Polymers are often two-phase composites, consisting of a matrix of one polymer with distributions of harder or softer particles contained within it. Concrete (the direct descendant of straw and mud bricks) is a classic example of a ceramic/ceramic composite, with particles of sand and aggregate of graded sizes in a matrix of hydrated Portland cement. These materials have been well known for many years, and materials scientists have learned to control their properties by controlling their microstructures; that is to say, the quantity, the shape and the distribution of what we might refer to as the 'reinforcing phase'. The idea of mixing components across materials class boundaries is a natural extension of this idea [9].

Composites are used not only for their structural properties but also for electrical, thermal, tribological and environmental applications. These features rely strongly on the specific constituents combined in the composite, on the extent of their presence in the final material (weight or volume fraction), and on the shape and architecture of the reinforcing phase. Ideally, the properties of engineering materials should be reproducible and accurately known. Since satisfactory exploitation of the composite principle depends on the design flexibility that results from tailoring the properties of a combination of materials to suit a particular requirement, the accurate prediction of those properties is imperative. At the present time, some of the more important engineering properties of composites can be estimated well on the basis of mathematical models, but many cannot

Decaying of the tooth is mainly due to the activity of bacteria. Different types of bacteria are found in the mouth; some of these are helpful, while some are harmful, which causes tooth decay. With sweet foods, these bacteria react and produce acids, and these acids remove mineral from enamel. Decay begins with enamel and goes deeper to dentine, and finally reaches to the pulp (nerve) of teeth, which creates cavities in the tooth over time. A decaying tooth causes pain, difficulty in eating, tooth loss, and inflammation around the tooth and gum. The human body has amazing properties for rebuilding injured parts; that is, if a bone fracture occurs, the human body heals the bone by developing new cells and joining them

are their high strength and stiffness, combined with low density, when compared with bulk materials, allowing weight reduction in the finished part [12]. In composites, materials are combined in such a way as to enable us to make better use of their virtues while minimizing to some extent the effects of their deficiencies. This process of optimization can release a designer from the constraints associated with the selection and manufacture of conventional materials. The designer can make use of tougher and lighter materials, with properties that can be tailored to suit particular design requirements [9]. The obtainment of tailored and desired properties cannot preclude specific manufacturing considerations. Indeed, the need to combine different materials appropriately and realize a well-defined product has a remarkable impact on the manufacturing processes that are suitable.

2.1.2 Dental materials

2.1.2. Teeth

Bones and teeth, the hard tissues in the human body, are made partly of organic and partly of inorganic material. The inorganic component mainly consists of a substance called hydroxyapatite - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. The outer layer of the teeth is the hardest material in human body and is called enamel. Enamel is a ceramic material that consists of approximately 92% hydroxyapatite. Beneath the enamel, the bulk of a tooth is made of dentin. This is a composite material and contains a mixture of hydroxyapatite, collagen, water, and salts. Collagen is an organic substance. Teeth function in one of the most inhospitable environments in the human body. They are subject to larger temperature variations than most other body parts and can cope with exposure to ice at 0 °C and to hot tea and coffee. Teeth also encounter pH changes in the range 0.5 to 8, as well as large mechanical stresses during chewing. Tooth decay, called caries, occurs when teeth are frequently exposed to foods containing carbohydrates (starches and sugars). Human teeth are not just aesthetic; they also play an important role in health and nutrition. Teeth prepare food for swallowing and digestion. Figure 1 represents the structural composition of the tooth.

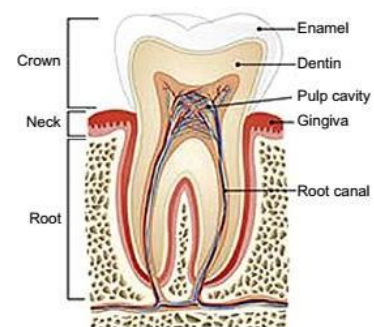


Figure 1. Tooth structure [13].

The light causes the monomer molecules to react with one another and link together to form a solid resin. The resin shrinks a little during polymerization so several successive composite layers are added and photocured. Photocuring is useful because it allows the dentist time to work with the material, building and shaping it correctly before it is exposed to light. When the dentist is ready, the filling can be hardened immediately by shining light on it. Finally, the filling is polished. Composite fillers have advantages and disadvantages. The table below summarizes these.

together. But this is not true in the case of teeth. Once a cavity is formed in a tooth, the human body cannot repair it. To repair a tooth cavity, a filling has to be done. With the help of a filling, dentists restore the damaged teeth back to their normal shape and function. Fillers have been used for a long time. Researchers have found around 7500–9500 years old molars with fillers in Pakistan. Recently, in Italy, scientists found a 6500-year-old tooth in which the filling was made up of bee’s wax [14]. It confirmed that fillers have been used for thousands of years. In the beginning of the 19th century, metal (gold, tin, silver, etc.) fillers were used. At the end of the 19th century, amalgam fillers were introduced. Amalgam fillers were made up of silver, mercury, tin, and copper.

Table 1 Advantages and disadvantages of using amalgam tooth filling [15].

Advantages	Disadvantages
<ul style="list-style-type: none"> Reasonably priced and cost effective Strong, resistant to wear and durable Dependable Least time-consuming kind of filling for a dentist to perform Average lifetime of amalgam fillers is about 15 years Used for more than a century with good results 	<ul style="list-style-type: none"> Silver color is no longer considered aesthetically acceptable (it is thought to look unpleasant) Does not stick to the tooth, which means the dentist has to make a large undercut cavity to keep the filling in place Conducts heat too well, which results in some people with amalgam fillers experiencing pain when they eat hot or cold foods Contains mercury (mercury compounds are poisonous) Getting rid of millions of potentially environmentally hazardous old fillers is a substantial disposal problem

2.1.5 Composite fillers

Composites used for filling teeth are generally made of silica or glass particles bound with a polymer resin. The polymers that are used as the resin in composites for fillers are based on a monomer called methacrylic acid. The polymer resin is usually filled with between 35 to 85% glass filler. The procedure used to place a composite filling in a tooth involves several steps. First, the tooth must be prepared. It is etched with acid to remove debris and an adhesive is applied. The solvent in the adhesive is then evaporated. Next, the cavity is filled with a layer of composite. This layer is hardened by shining a light on it – a process called photocuring.

2.1.6 Dental composite materials

The majority of matrix materials that exist on the composites market are polymer. There are several different polymer matrices which can be utilized in composite materials. Among the polymer matrix composites, thermoset matrix composites are more predominant than thermoplastic composites. Though thermoset and thermoplastics sound similar, they have very different properties and applications. Understanding the performance differences can help to make better sourcing decisions and the product designs as composites [16].

2.1.4 Glass ionomer fillers

Glass ionomer fillers are similar to composite fillers because they also use a polymer resin. However, the filling material contains strontium, phosphate and fluoride ions. The big advantage of this filling material is that it interacts with the enamel and dentin in the tooth and forms an excellent seal between the filling and the tooth. A true biological and chemical link is formed with the tooth and this reduces the sensitivity of the filled tooth. Another advantage of glass ionomers is that the fluoride ions from the filling material are continually released by reaction with saliva. These fluoride ions are next to the teeth and can react with the enamel. This helps strengthen the teeth and prevent further decay. The disadvantages of glass ionomer materials are that they are not as aesthetic as composites and they are weak under normal chewing forces.

Table 2 Advantages and disadvantages of composite fillers[15].

Advantages	Disadvantages
Color and texture can be matched to the patient’s teeth by the addition of different fillers	Less durable than amalgam and not strong enough to withstand the chewing forces in the back of the mouth
May be used to change tooth color, shape and size to improve the smile	Subject to shrinkage and loosening when the material sets, which leads to formation of a small gap between the tooth and filling
Does not contain mercury	Cannot be used for large fillers
Very useful for front teeth and small holes in the back teeth where the biting load is not too great and appearance is crucial	Wears out faster than amalgam
Less tooth has to be removed to provide a key for the filling than is necessary with amalgam fillers	If the coating is too thick, the polymer may separate from the tooth surface during the setting process, which weakens the bond between the filling and the tooth
	The acid-etching technique removes minerals from the dentin in the tooth and can weaken it
	Dental caries and composite fillers have poor X-ray contrast with their surroundings, which makes it hard for the dentist to identify new areas of decay
	Filling a tooth using composites is a more precise procedure and takes longer to perform than inserting an amalgam filling; composite fillers may therefore cost more

Thermosets are materials that undergo a chemical reaction or curing and normally transform from a liquid to a solid. In its uncured form, the material has small, unlinked molecules known as monomers. The addition of a second material as a cross-linker, curing agent, catalyst, and/or the presence of heat or some other activating influences will initiate the chemical reaction or curing reaction. During this reaction, the molecules cross-link and form significantly longer molecular chains and cross-link network, causing the material to solidify. The change of the thermoset state is permanent and irreversible. Subsequently, exposure to high heat after solidifying will cause the material to degrade, not melt. This is because these materials typically degrade at a temperature below where it would be able to melt. Thermoplastics are melt-process able plastics. The thermoplastic materials are processed with heat. When enough heat is added to bring the temperature of the plastic above its melting point, the plastic melts, liquefies, or softens enough to be processed. When the heat source is removed and the temperature of the plastic drops below its melting point, the plastic solidifies back into a glasslike solid. This process can be repeated, with the plastic melting and solidifying as the temperature climbs above and drops below the melting temperature, respectively. However, the material can be increasingly subject to deterioration in its molten state, so there is a practical limit to the number of times that this reprocessing can take place before the material properties begin to suffer. Many thermoplastic polymers are addition-type, capable of yielding very long molecular chain lengths or very high molecular weights [17].

Both thermoset and thermoplastic materials have its place in the market. In broad generalities, thermosets tend to have been around for a long time and have a well-established place in the market, frequently have lower raw material costs, and often provide easy wetting of reinforcing fibre and easy forming to final part geometries. In other words, thermosets are often easier to process than thermoplastic. Thermoplastics tend to be tougher or less brittle than thermoset. They can have better chemical resistance, do not need refrigeration as uncured thermosets (prepreg materials) frequently do, and can be more easily recycled and repaired. Dental composites were developed in 1962 with dimethacrylates, combined with powdered silanized quartz [18]. Composites have replaced the amalgam due to their unique properties (aesthetic and adhesive properties). Today, composites are used globally as tooth-colored restorative materials. Composites are generally made up of three components: organic materials (resin matrix), inorganic materials (fillers), and coupling agents. Figure 2 represents the classification of dental filling composite materials.

3. Materials

For polymer matrix mostly the commercial acrylic denture resins were used. Commercial acryl denture material „Simgal-Acryl R”, Galenika AD, Belgrade, Serbia, was used as a autopolimerized acrylic resin [47, 54]. "It is a two-component system consisting of a powder and a liquid. The powder consists of a PMMA copolymer and the initiator benzoyl peroxide (BPO) in a concentration of 1.1% w/w. The liquid was made of methyl methacrylate (calc) 94.15% w/w; acid as methacrylic acid 19.8 ppm w/w; *N, N*-dimethyl-*p*-toluidine as accelerator 0.85% w/w; ethylene glycol dimethacrylate as cross-linking agent 5.00% w/w;

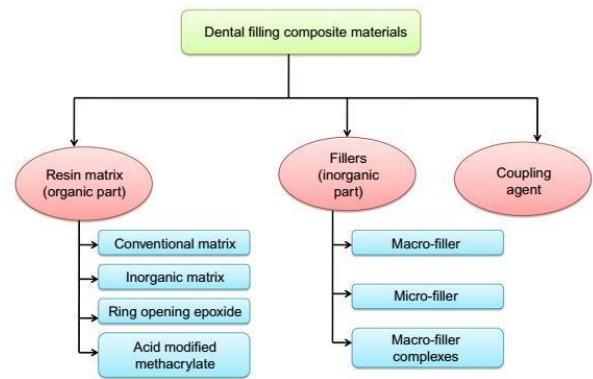


Figure 2: Classification of dental filling composite materials [19].

2.2 Experimental for hybrid denture composites

From review of some experimental research it is evident that for some systems of hybrid reinforcement's design of mechanical properties is possible with the proper combination of constituents according to exploitation requirements "Hybrid reinforcement systems have been created previously to develop mixtures of different fibers, metal oxides, or fibers and fillers reported to produce improvements in the physical properties compared to adding them separately" [50].

Table 3. Performance parameters comparison of the literature data

	Matrix	Reinforcements	Mechanical properties	Reference
1.	Acrylic Denture Base Material	1% Silanized zirconium oxide (ZrO ₂) nano filler and 2.5 %electrospun PS fibers	Absorbed Impact energy improvement 70 %, Hardness improvement 10 %	[47]
2.	Acrylic Denture Base Material	Silanized zirconium oxide (ZrO ₂) nano filler and plasma treated polypropelene (PP) fibers	tensile strength, improvement 44%	[48]
3.	PMMA	PP fibers 2.5 t. %)/Al ₂ O ₃ nanoparticles (1 wt. %)	Impact strength improvement 119% Surface hardness improvement 4.2%	[49]
4.	Denture base PMMA	ZrO ₂ -Al ₂ O ₃	Tensile strength decrease 17.0% (highest value for 100% ZrO ₂) Fracture toughness improvement 32.5% (ZrO ₂ /Al ₂ O ₃ =20/80)	[52]
5.	Denture base PMMA	ZrO ₂ /Aluminum borate whiskers	Surface hardness improvement 26.4% (reinforcement ratio 1:2, 3% ZrO ₂) Felxural strength improvement 52.3% (reinforcement ratio 1:2, 2% ZrO ₂)	[53]
6.	Denture base PMMA	Glass/UHMW PE fibers in form of fabrics 5.3%	flexural strength 90% and modulus 76%	[54]
7.	Acrylic Denture Base Material	Alumina whiskers and PS fibers with Grubs catalist	Self healing composite with 74% healed impact energy	[55]

water 27 ppm w/w. In the other studies also used auto polymerized and thermo polymerized acrylic resins." [47, 54].

As ceramic nano filler in the composite mostly used nanopowder of ZrO₂ (with a particle size ~100 nm), Sigma Aldrich, was used as particle reinforcement [47, 48, 55]. Also the alumina whiskers were commercially available from Sigma–Aldrich, and they were characterized by diameters of 2–4 nm and lengths of 200–400 nm (specified by the producer) and Aluminum borate whiskers [52, 564]. For surface modification of zirconia 3-Methacryloxypropyltrimethoxysilane (MEMO) (Dynasylane, Evonik Industries) was used [47, 48, 54], while for modification of alumina 3-mercaptopropyltrimethoxy silane (MPTMS, 95 %; Sigma–Aldrich.) was used as a coupling agent [52, 55].

Polystyrene (PS) used to obtain electrospun fibers and PS fibers with Grubs catalyst was purchased as Empera1251N from Ineos Nova. Solvent for PS solution was 99.8% dimethylformamide (DMF), purchased from Sigma-Aldrich [47, 55]. "Electrospinning (Electrospinner CH-01, Linari Engineering) was performed with a 20 ml plastic syringe with a metallic needle of 1 mm inner diameter set vertically on the syringe pump (R-100E, RAZEL Scientific Instruments) with 15 cm distance from the needle tip to the collector, and the high-voltage power supply (Spellman High Voltage Electronics Corporation, Model: PCM50P120) set to a voltage of 28 kV at the room temperature (25°C) and the humidity of 47%. The flow rate of the polymer solution was 5.0 ml/h. The concentration of PS in DMF solution prepared for electrospinning was 22 wt. %." [47, 55]. The polypropylene fiber (Crace cemfiber) cutted to 4.0 mm length and modified by oxygen plasma was also used in hybrid composite [48]. In yhe other study glass fibers -GFs (E-glass, Shanghai Richem International Co., Ltd.) 3mm length and 12 μm diameter [50].

3.1 Methods of Characterization

"The microstructure of the composites was studied by SEM microscopy/ Image analysis was performed by Image Pro-Plus 4.0 software (Media Cybernetics) that provided the information about PS fiber diameter distribution." [47, 55]

"Fourier transformed infrared (FTIR) analysis was performed to investigate bonding between nanoparticles and the matrix."

"Mechanical characterizations of the samples were performed by Vickers microhardness (HV) tester, Impact test was performed using Puncture Impact testing machine HYDROSHOT HITS-P10. Tests were performed on five specimens according to the ASTM D 3763–15, and the results were presented as mean values with standard deviations. The data were analyzed in terms of the maximum load, energy corresponding to the maximum load and total energy." [47, 55].

A pendulum Charpy-type impact test machine (Digital Charpy Izod

observed at 1173 cm⁻¹ in the spectrum of modified zirconia. The peak at 1721 cm⁻¹ that is associated with carbonyl stretching band C = O which is present in the silane coupling agent (MEMO) was observed in the spectrums of modified zirconia and the composite (shifted to 1733 cm⁻¹). The presence of adsorbed water was confirmed by the Zr–H₂O flexion at 1635 cm⁻¹. " [47].

impact tester, XJU 5.5, Jinan engrand Instrument Co., Ltd.) was used to perform the impact test at room temperature" [50]

"For tensile strength flat dumbbell shaped with (75mm in length, 4.0mm in width and 2.5mm in thickness) at the parallel segment. Dumbbell shaped specimens were fabricated according to ASTM specification D-638M (1986). Instron universal testing machine (LARYEE, china) where used to accomplished the test with crosshead speed 1.0 mm/min and maximum loading of 20 Kg." [48]

"For the flexural strength test, the specimens were bar-shaped with dimensions of 65 × 10 × 2.5mm ± 0.2mm according to American Dental Association (ADA) Specification No. 12." [50].

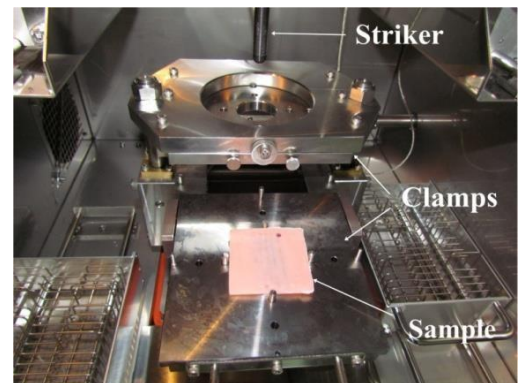


Figure 3. The sample in machine for impact test [56]

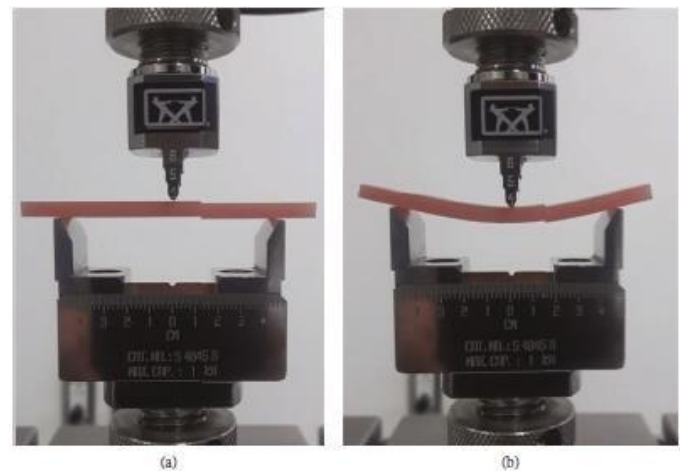


Figure 4: (a) Flexural strength of the specimen placed on the universal testing machine and (b) specimen subjected to bending strength until failure load recorded with specimen fracture. [50].

4 Results and discussion

4.1 FTIR analysis

The FTIR analysis was used to identify possible establishment of chemical bonding during processing of hybrid polymer composites. Also, it is important to prove the chemical modification of nanoparticles surfaces.

"The FTIR spectra of both unmodified and modified zirconia nanoparticles and the composite with modified zirconia are presented in Fig 12a. All spectra have a peak at 754 cm⁻¹ that is attributed to Zr–O stretching vibrations at ZrO₂ nanoparticles. Characteristic acrylate CH₃ vibration of MEMO silane was

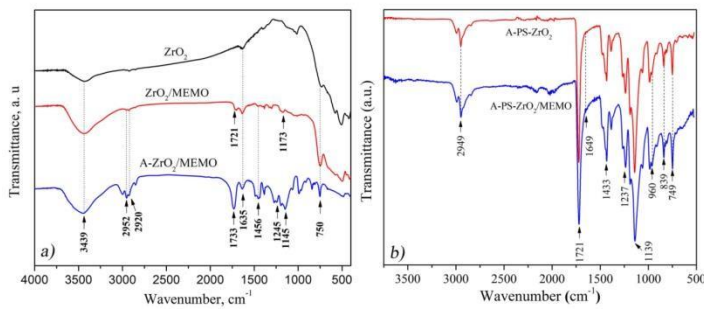


Figure 5 "FTIR spectra of: a) neat ZrO₂ particles, ZrO₂ particles modified with MEMO silane and a composite reinforced with ZrO₂/MEMO and b) hybrid composites A-PS-ZrO₂ and A-PS-ZrO₂/MEMO"[47]

"FTIR spectra of A-PS-ZrO₂ and A-PS-ZrO₂/MEMO is presented in Fig 10b. All the spectra have peaks in the region of 2995–2840 cm⁻¹, which are assigned to the stretching of the C–H bonds contributed mostly to PMMA and PS. The peak at 749 cm⁻¹ is attributed to Zr–O stretching vibrations from nanoparticles in all the spectra. Double bond C = C stretch which is sensitive to ring strain vibration at 1649 cm⁻¹, indicated conjunction with the phenyl group in PS, emphasized with MEMO silane. An increased intensity of the signal at 960 cm⁻¹ in A-PS-ZrO₂/MEMO compared to A-PS-ZrO₂ indicates the formation of Si–O–Zr bond." [47]

"The silanization of whiskers was followed by the FTIR spectrum of unmodified and modified whiskers (Fig. 2). The FTIR spectrum of MPTMS silane is also presented on Fig.13."

"The band at 2560 cm⁻¹ observed in the spectrum of WMPTMS is assigned for the S–H stretch band [26, 30], which was not observed in the absorption spectrum of un8]. The absorption bands for the propyl group are appearing at 2936 and 2852 cm⁻¹ due to the C–H stretching vibrations, further justifying the MPTMS anchored onto whiskers. Additionally, the band in the 1075 cm⁻¹ is assigned to the vibration of Si–O–Al bond [59, 60]. These facts indicate that chemical immobilization of MPTMS on nano whiskers was successfully occurred [60, 61]."[55].

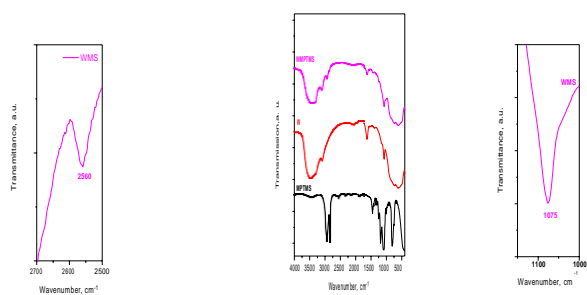
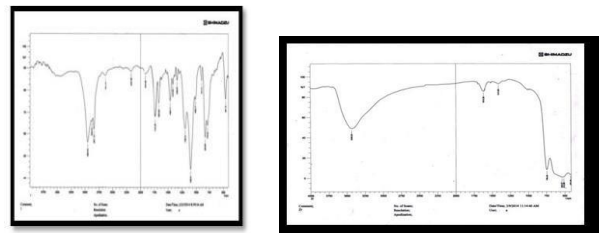


Figure 6. FTIR spectrum of MPTMS silane, whiskers (W) and silanized whiskers (WMPTMS). The enlarged parts are from WMPTMS spectrum"[55]

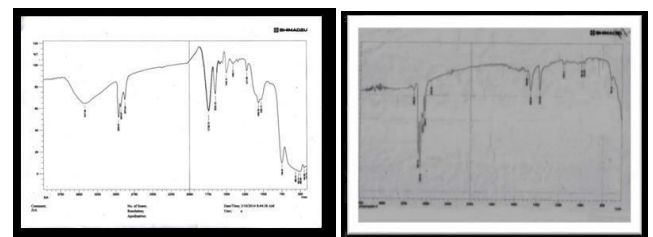
"The characterization FTIR test has performed to samples of zirconium oxide nanofiller before Silanization which mean without modification, and (trimethoxysilyl) propyl methacrylate (TMSPM) silane coupling agent to indicate the difference in the spectra, as seen in figure (4) and figure (5) below. Additionally other FTIR has performed to zirconium oxide nanofiller after Silanation to indicate the differences in in the peaks, as seen in Figure 14. MPS absorption bands could be assigned to functional groups presence." [54]

4.2 FE-SEM analysis

Morphology and size of hybrid reinforcements could be observed by FE-SEM analysis. "The size distribution of PS fibers was obtained using image analysis tools and the results are presented in Fig 15. PS diameter distribution with mean diameter $D_{mean} = 1.51 \mu\text{m}$ (standard deviation = $0.52 \mu\text{m}$) was best fitted with the Lognormal distribution curve. FE-SEM images of cross-sections of the polymer after the impact testing are presented in Fig 16. Shows that zirconia agglomerates observed in the sample with unmodified particles had larger diameters and consisted of a larger number of individual particles, (Fig 16a) while surface modification of nanoparticles with MEMO silane (Fig 16b) enabled aggregates to be smaller in diameter and more evenly spaced. In Fig 16c and 16d the areas with fibers are presented. The modification of nano zirconia with MEMO silane produced a monolayer of silane on the surface of the particles, and promotes deagglomeration in the polymer matrix because of the steric hindrance." [47].



FTIR spectrum of TMSPM FTIR spectrum of non silanized zirconium oxide nanoparticles



FTIR spectrum of zirconiananoparticlesaftersilanization FTIR of untreated PP fibers

Figure 7. FTIR analysis of established bonding during modification of reinforcements in hybrid composites[48].

"SEM view of the group D specimens (Figure 8(a)) showed the roughest surface among all the reinforced groups, glass fibers failed adhesively at the plane of the fracture and protruded, voids formed due to the glass fibers that were pulled out were higher in number than group C.

SEM image of group E specimens exhibited a similar morphology to that seen with group C, but the fibers were completely protruding out of the fractured end with voids on the opposing surface of the specimens (Figure 5(b)). As expected, a considerable number of GFs were seen on the surface of the specimens of groups F and G (Figures 8(c) and 17(d))."[50]

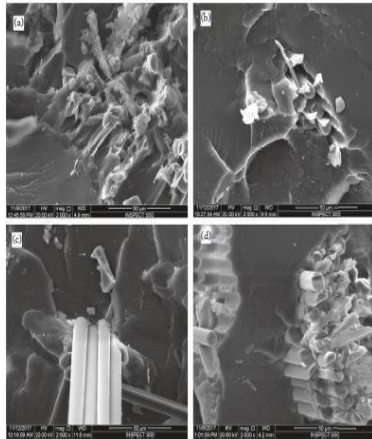


Figure 8: SEM of fracture surfaces of flexural test specimens. (a) 2.5% nano-ZrO₂ + 2.5% GFs; (b) 2% nano-ZrO₂ + 3% GFs; (c) 1% nano-ZrO₂ + 4% GFs; (d) 0% nano-ZrO₂ + 5% GFs.[50]

4.3. Mechanical properties

4.3.1. Hardness test

"Vickers hardness test reflects the uniformity of reinforcement dispersion in the composites and its resistance to shear stresses under local volume compression. Table 2 presents Vickers values for the PMMA matrix and the composites. The addition of 1 wt. % zirconia nanoparticles improved microhardness by 3%. In composites with silanized zirconia (ZrO₂/MEMO) the effective dispersion and cross-linking was achieved, and thus improvement of HV value of 29% for 1 wt. % modified zirconia resulted. On the other hand, the introduction of PS fibers leads to lower hardness values. The PMMA and PS are immiscible and don't interact easily. Added PS fibers didn't interact with the PMMA paste during the preparation of the composite. This leads to interfacial tension in those areas which is followed by attraction of nanoparticles in the vicinity of PS fibers. This influence of the composites' mechanical behavior of leads to lower hardness and T_g. In order to emphasize the influence of different nanoparticle concentrations in the hybrid composites, samples with 0.5 wt. % of MEMO silane functionalized ZrO₂ nanoparticles were also subjected to micro Vickers test. The hardness growth trend remained the same—nanoparticles ZrO₂/MEMO offer improved hardness due to higher compatibility of MEMO functional groups with PMMA matrix. The presented results revealed that the hardness could be adjusted by optimizing the content ratio of modified zirconia and PS fibers." [48]

Table 4 Results of Vickers hardness test for hybrid composite PMMA-ZrO₂-PS fibers [48].

Sample	HV, MPa	St.dev., MPa
A	243	±1
A-ZrO ₂	250	±5
A- ZrO ₂ /MEMO	313	±8
A-PS	211	±5
A-PS-ZrO ₂ -1.0	229	±8
A-PS-ZrO ₂ /MEMO-0.5	232	±1
A-PS-ZrO ₂ /MEMO-1.0	269	±3

4.3.2 Impact test

"The position of a sample in the impact machine and samples before and after the impact test is presented in Fig 18. The results of the controlled energy impact test are presented in Fig 19. The impact behavior of the hybrid nanocomposites with PS fibers and modified particles was significantly improved, compared to the pure PMMA.

"The flexural strength of group G (0% nano-ZrO₂ + 5%GFs) nanocomposites was elevated by 6% when compared to that of pure

Table 4. presents the absorbed energy values. Absorbed energy is defined as the energy difference between the total energy and the energy at peak load. As the composite materials are brittle, it was assumed that energy up to the peak load was due to the elastic deformation of the sample and that beyond the peak load, energy was spent on creation and propagation of cracks. As expected, sample A-PS showed the highest ability to absorb energy during the impact, almost 92% higher than the pure PMMA. FE-SEM analysis showed the difference in the observed matrix-PS fiber interface after the impact test. Acrylic resin with PS fibers has a clear and smooth surface that indicates poor contact between the two polymers (Fig 20a). In the case of a matrix with unmodified ZrO₂ particles, it could be seen that particles built some agglomerates (Fig 20b) at PS surface and slightly improved contact between the fibers and the matrix. Surface modification of ZrO₂ particles with MEMO silane significantly improved the compatibility of the interfaces in a hybrid composite A-PS-ZrO₂/MEMO (Fig 20c). Modified composite matrix (A-ZrO₂/MEMO) filled the space between the fibers and improved the contact between the matrix and the fibers." [48]

"Incorporation of pure brittle zirconia, prone to agglomeration, reduced absorbed energy, while it was successfully compensated latter with the combination of modified particles and the electrospun polymer fibers. Therefore, sample A-PS-ZrO₂/MEMO-1.0 shows the value of total absorbed energy close to the one of A-PS, and the shape of failure mode which is, following the assumption, based on FE-SEM analysis." [48].

4.3.3 Flexural test

Mean values, standard deviations, and statistically significant differences of flexural and impact strengths are summarized in Table 3, addition of different concentrations of nano-ZrO₂ + GFs significantly increased the flexural strength for all reinforced groups when compared to the control group (p < 0.05). Different ratios of nano-ZrO₂ + GFs resulted in varied effects on the flexural strength of the composite material.

Table 5. Tukey–Kramer multiple-comparison test for flexural strength (MPa) and impact strength (kJ/m²) of denture base resins showing mean ± SD and groups with significant differences [50]

Groups	Flexural strength (MPa) Mean ± SD	Impact strength (kJ/m ²) Mean ± SD
Control	64.52 ± 5.76	3.89 ± 0.46a
A	75.16 ± 6.95a	3.80 ± 0.71b,c
B	77.63 ± 5.65a	3.44 ± 0.82b
C	85.82 ± 6.96b	3.30 ± 0.65c,d
D	94.05 ± 6.95	3.24 ± 0.64d
E	83.28 ± 5.32b	2.77 ± 0.92b
F	75.55 ± 6.23a	2.37 ± 0.46e
G	68.21 ± 7.76	1.99 ± 0.63a,e

"The results showed that the flexural strength of group A (5% nano-ZrO₂ + 0% GFs) nanocomposites was elevated by 21% when compared to that of unreinforced PMMA. The good distribution of the very finely sized nano-ZrO₂ used in the study enabled them to occupy the spaces between linear chains of the polymer, thereby restricting the segmental motions of the macromolecular chains and increasing strength and rigidity of the resin. This mechanism enhanced the fracture resistance and improved flexural strength." [50]

PMMA. When the load is applied on the specimen, tension occurs below the long axis of the specimen. The high modulus of elasticity of GFs as well as the strong bond between the matrix and fibers leads to hindrance of crack initiation and propagation under the failure load; resist tension occurs below the long axis of the specimens, subsequently increasing the flexural strength.”[50]

Conclusion:

Organic-inorganic nanocomposites have wide application in dentistry and prosthetics. Inorganic materials play a key role in sustaining and supplementing mechanical properties of polymer matrices and in further favoring cellular behaviors. As a result, in dentistry, biocompatible nanocomposites are able to be substituted for native tissue as shown in many clinical cases. Hybrid polymer composite materials show improved mechanical properties coming from a synergy of different reinforcements. Ceramic nanoparticles, which possess appropriate surface modification; and non-woven polymer fibers are proven to be good candidates for incorporation in the acrylic matrix to successfully modulate of mechanical and thermal properties of the hybrid nanocomposite material. Interactions between the fibers and the matrix were strong enough to allow load transfer from the matrix to the fibers, which ensured better mechanical properties of the processed hybrid nanocomposite. The interfacial adhesion strength between the matrix and the fibers increased resistance to crack generation and propagation. These failure mechanisms led to the high absorption of impact energy as a consequence of dissipation during crack propagation. These results show that dental materials can be modified to withstand higher impact force and to have excellent elastic properties and high biocompatibility at the same time. However, most biocompatible nanocomposites still lack the data for clinical applications when compared to data of monophasic resin. Further in vivo or clinical studies are imperatively needed for use of bionanocomposites in dental applications.

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