Preparation and characterization of Novel Bis-GMA Dental Nanocomposite and their application as dental material: Mechanical Properties and Water Sorption/volumetric shrinkage

Mohammed Ali Mutar¹, Israa Faisal Ghazi², and Mahdi Saleh Mahdi³

¹,³ Chemical Engineering Department, College of Engineering, University of Al-Qadisiyah, Iraq
²Materials Engineering Department, University of Technology, Iraq
*mohammed.ali.@qu.edu.iq; Mohammeddw73@gmail.com

Abstract. Novel Nanocomposite materials on the basis of unsaturated monomers as well as 2,2 propyl bisphenol glycidyl dimethacrylate (Bis-GMA) and unsaturated monomers with Nano inorganic fillers [SiO₂, ZrO₂ and Hydroxyapatite (HA)] were subjected to process of synthesizing as well as characterizing for the purpose of evaluating their possible applications as restorative materials in the field of dentistry. The initial method has been for generating in addition to characterizing novel Nanocomposites bases on (Bis-GMA), N,N′-methylene bis acrylamide (MBA), acrylic acid(AA) and methylacrylate(MA) monomers. Composites containing Bis-GMA and N,N′-methylene bis acrylamide (MBA) with the ratio (wt / wt) of (40 / 20), which has been filled with various Nanofiller amounts (up to 5% wt) were prepared. Photo-polymerization has been induced with camphorquinone / N,N -Dimethylaminoethyl methacrylate CQ / DMAEMA), as photo-initiator system. Physicochemical properties, such as solubility (SL), water sorption (WS), as well as the volumetric shrinkage (VS) have been examined. The mechanical properties of the of dental Nanocomposites flexural strength and compressive were widely discussed. Characterization will be implemented through the use of FTIR and SEM are applied for showing particle size distribution in addition to particle agglomeration related to the treated Nanofillers in Nano-composites. FTIR spectroscopy has been initially applied for identifying qualitative composition of composition of Nanocomposites. The Thermal stability of all dental Nanocomposites were also studied using the TGA and DSC techniques.

1. Introduction
The dental processes have become simple and palatable because of the advancements in bonding technologies as well as the tooth-colored restoratives[1]. Restorations matching the natural teeth’s color are the major requirements for patients. Such demands are fulfilled with the resin composites as they became the major applied esthetics materials in the dentistry field[2]. Furthermore, the mercury controversy is avoided via the composites, also they utilize adhesive systems for bonding to tooth structure. Composites are considered to be as multi-phase materials which shows the characteristics of the two phases (inorganic as well as organic) in which phases are complimentary, leading to materials with improved features[3, 4]. Compositions that are related to the resin-based dental composites have been considerably improving starting from when they have been initially used in dentistry filed over...
five decades ago. In the year 1951, Oscar Hager (Swiss chemist) introduced the initial dimethacrylate molecule, that enabled cross-polymerized matrix.

Rafael Bowen, in the year 1962, introduced large molecules, hydrophobic dimethacrylate monomer (Bowen’s resin or Bis-GMA), a major improvement in the resin chemistry field. Due to their fracture resistance as well as limited shrinkage, Bis-GMA are of high importance in the current composites. The amount of filler particles which could be incorporated are limited because the honey’s viscosity of Bowen’s resin. Following studies involved N,N Methylene Bis acrylat amide (N,N MBAA) as diluent for reducing the viscosity. To this day, such monomer combinations are considered to be majorly applied matrix monomer combinations in the dental composites.

The two of the monomers include 2 reactive double bonds, when they are polymerized, form covalent bond between the chains of polymers referred to as crosslink. The physical as well as mechanical characteristics are improved via crosslinking[5]. In 1969, it has been initially applied in composites. Resin composites are majorly utilized as posterior as well as anterior filling materials. Also, products that have comparable composition have been utilized as pit and fissure sealants, for buildups and cores, luting composites, bridges and temporary crowns, inlays, on lays, root canal posts, root canal sealers, in addition to bonding regarding brackets and orthodontic bands[6]. Due to their versatility, resin composites will be used widely and frequently in many applications.

The main aim of the presented study is synthesizing and characterizing the new composite dental materials, with the use of recently synthesized dental Nano composite, with inorganic phase content of range 0.2, 0.4, 0.6, 0.8, and 1.0% (wt). The applied monomers have been Bis-GMA, MBA, as well as unsaturated monomers such as (AA and MA) . The benefits of applying Bis-GMA Nanocomposites are high mechanical characteristics, reduced shrinkage, rapid hardening through free-radical photo-polymerization,[7, 8] thermal stability and decreased toxicity because of to its diffusivity into tissues as well as their lower volatility.[9-11]

2. Experimental

2.1. Materials

Methacrylate(MA) (MERCK), Acrylic acid (AA) (HIMEDIA), 2,2 propyl bisphenyl glycidylidimethacrylate (BIS-GMA)(USA), N,N Methylene Bis acrylat amide (MBA)( Aldrich), Zinc Oxide (ZnO)( GCC), Zirconium Oxide Nanoparticles (ZrO2)( Skyspring Nanomaterial), Silicon Oxid Nanoparticles (SiO2)( Skyspring Nanomaterial), Nano Hydroxyapatite (HA)( Skyspring Nanomaterial), 2-(Diethyl amino)ethyl acrylate(ALDRICH), Camphorquinone(ALDRICH).

2.2. Apparatuses

Digital Sensitive Balance, Sarorius, Bl210s, Germany, Mixer, Scanning Electron Microscopy (SEM)(JEOL,Japan), FTIR TENSOR 27, Fourier transform infrared spectrooscope, BRUKER, Germany., (Thermogravimetry analysis (TGA) were performed on a polymer laboratories co England, Model pL-TG at Iran polymer & petrochemical institute, using a heating rate of 10ºC/min in Argon atmosphere within the temperature range of (25-800ºC) (differential thermal analysis (DSC) measurement using apparatus (DSC) type (DSC 131 Evo, SETARAM) is the origin (France) in the college of education for pure science Ibn – AL Haitham central service laboratory/University of Baghdad. properties were measured using a tensile testing machine from ( LARYEE Co)/ China. With a load cell of 20 kN and a cross-head speed of 200 mm/min at room temperature. The sample dimensions were accordance to ASTM D-412.

2.3. Fabrication of Experimental Dental Nano-composites (A1-A3)

The experimental dental Nano-composites have 2 series, which have been subjected to a process of fabrication through mixing fillers as well as the monomer matrix. Monomer matrix (Bis-GMA, MA, AA, and (MBA) has been subjected to mixing process in the mass ratio (40/20/20 and 20) for one hour. After that, a process of adding the zinc oxide (0.5gm) as antimicrobial agent has been implemented, also
a process of adding Nanofillers (0.7gm) as colorant has been also implemented for improving the mechanical characteristics. After that, a process of adding DMAEMA (0.5wt%) as accelerator and camphorquinone (0.5wt%) as initiator has implemented and continuous for twenty minutes. Then, the paste has been inserted to the test moulds and the light cured with the use of a light curing unit (EliparFreelight2LED, 3 M ESPE) at 1500 mW/cm² intensity. Light has been illuminated on the two surfaces, bottom and top, via clear matrix strips for forty seconds. Since it is majorly applied via clinicians, curing time of forty seconds has been applied for curing the experimental Nano-composites. Tip distance that is related to light curing unit has been kept at 1–2 mm from the surface of the surface. The concentration of materials is explained in table 1.

### Table 1: Monomers and photo initiators used in this study

| Sample No. | Bis-GMA (%) | MA (%) | AA (%) | MBA (%) | Nano fillers (0.7 gm) | Photo Initiator | Accelerator |
|------------|-------------|--------|--------|---------|-----------------------|-----------------|-------------|
| A1         | 40          | 20     | 20     | 20      | SiO₂ Nano            | 0.5 wt.%        | 0.5 wt.%    |
| A2         | 40          | 20     | 20     | 20      | ZrO₂ Nano            | 0.5 wt.%        | 0.5 wt.%    |
| A3         | 40          | 20     | 20     | 20      | Hydroxyapatite Nano  | 0.5 wt.%        | 0.5 wt.%    |

2.4. The Process of Curing

The monomers have been mixed with: 0.4wt% camphorquinone (CQ, Sigma-Aldrich)—the photosensitizer—and 1wt% N,N-di-methylaminoethylmethacrylate (DMAEMA, Sigma-Aldrich)—the reducing factor—and with vigorous stirring, poured to moulds—Petri dishes (with a diameter of 120mm and thickness of 4mm). Those samples have been covered by PET film for the sake of reducing the impacts of the inhibition of oxygen and after that, irradiated, at a room temperature, for half an hour. Photo-polymerization has been started by a mercury vapor lamp of high pressure (FAMED1, model L6/58, Lodz, Poland, power 375W[12, 13]), which emits Ultra-Violet/VIS light, where camphorquinone is absorbed in a range between 420nm and 500nm[14].

2.5. Measurement of Volumetric Shrinkage (VS)

The VS related to dental resins has been examined via the variations in density pre and post the process of photo polymerization, also, the Archimedes principle has been used to determine the density. Measurement has been implemented with the use of commercial Density Determination Kits related to the analytical balance Mettler ToledoX on basis of ISO17304:2013 (E).

2.6. Measurement of Water Sorption (WS) and Solubility (SL)

Water sorption (WS) and solubility (SL) have been acquired on the basis of ISO4049[15].

2.7. Scanning Electron Microscopy (SEM)

Researches on the Morphology have been carried out on the cured materials’ fractured surfaces with Hitachi TM3000 SEM, Tokyo, Japan. Sample surfaces, prior to observations, have been sputter coated in gold.

2.8. Physico-mechanical properties of the test samples

2.8.1. Flexural characteristics. The flexural strength (σ) and the flexural modulus (E) have been specified according to the ISO178.

2.8.2. Compression set. Compression set was measured according to ISO 1653 at ambient temperature.

3. Results and Discussions
3.1. Prepared Polymers Synthesis and Characterization

3.1.1. Synthesis and FTIR spectrum of (A)
The preparation of polymer (A) has been done via co-polymerization process that is related to the MA, AA, Bis-GMA, with cross-linker (MBA), in the presence of camphorquinone as photo initiator and N,N-dimethyl aminoethyl methacrylate as accelerator the reaction was continued through a process of mixing for 40 minutes and at room temperature under N2 gas for the purpose of removing dissolved oxygen, just as can be seen in reaction scheme (1):

![Scheme 1. Synthesis of polymer (A)](image)

**FTIR analysis**
There are many bands related to the infrared spectrum, majorly the wide range in range of (3300 - 3450) cm⁻¹, that indicate overlaps the current absorption (OH). Appearance of the beams in range of (2850 - 2990 cm⁻¹) to vibratory vibration that is related to aliphatic CH bonds in polymer’s structure. Characteristic beams at 1750 cm⁻¹ indicate (C=O) of acid’s group, moreover, characteristics beam at 1725 cm⁻¹ indicate the (C = O) vibration of ester group, aromatic (C=C) are indicated at range of (1475 - 1600 cm⁻¹).Characteristic bands in range of (1390 – 1400 cm⁻¹) are the result of (C – Н) bonds for the (CH3) group of polymers. The absorption bands in range of (1000 - 1100 cm⁻¹), (C – О) [18,19], as can be seen in Figure 1:

![Figure 1. FTIR spectra for (A)](image)
3.1.2. Water Sorption and Solubility (WS)
Water sorption (WS) and solubility (SL) have been acquired on the basis of ISO4049[15]. Steel split mold has been utilized for making the specimens with diameter of (15 millimeter) and (1 millimeter) thick (n=5). WS has been decreased through using extra hydrophobic monomer, preventing the hygroscopic expansion. Water sorption might be accounted for the adverse effects such as discoloration and subsequent swelling of restorative materials.

With regard to the presented study, there has been an increase in the water sorption with the reduction in conversions of the tested formulation. Because of their molecule’s hydrophobic character, as well as the elevated conversion, Bis-GMA presented with the lowest water sorption[16]. With regard to the N,N MBAA, elevated conversions do not translate to elevated cross-linking density, as mentioned earlier, thus second to last lowest water sorption has been fairly unpredicted[17], also it should be associated with its low hydrophilicity in comparison to Bis-GMA. Very comparable water sorption values have been shown by hydrophobic monomers and Bis-GMA, despite differences in the conversion, possibly due to the fact that these are considered to be the major hydrophilic molecules assessed in the presented study.

In addition to being dependent on hydrophilic character and amount of leachable in products, the results of solubility are on the basis of amount of water absorbed in network. Furthermore, the pendant double bonds which are contributing to greater free volume to network[18] and favor WS, could not be contributing to the leachable species (oligomers and monomers), due to the fact that they’re tied to network. This might explain the reason behind solubility values being related to Bis-GMA have not been greatest among homopolymers, regardless of its considerably more elevated WS. N,N MBAA, at the same time, because of tendency to cyclization, indicated the highest results of SL, despite low water sorption and high conversion, probably due to the fact that the oligomers of low-molecular-weight have been existent and ready for leaching. The low SL results from the Bis-GMA have been clarified through the hydrophobic character as well as the high conversion (with regard to this condition, possibly also with greater cross-linking) of molecule. Also, it must be indicated that the results of SL could be undervalued for more hydrophilic monomer, due to the fact that the water yield stronger hydrogen bond interaction with the hydroxyl and (in Bis-GMA), as well as weak bond with the ethylene glycol unit (which are presented in great concentrations in N,N MBAA), the could be hindering the water elimination throughout the 2nd period of storage in desiccators[17]. It appears that the distinct characteristics which are related to tested dimethacrylate homopolymers are the cause of their unique behavior with regard to the flexural properties, polymerization kinetics, WS and SL. These properties explain using the co-polymers for the purpose of obtaining high DC and mechanical characteristics, in addition to optimum resistance to water degradation.

It can be indicated that, the before water immersions Bis-GMA-based resin had similar after water immersions, which can be an indication of its more effective water resistance. WSL reveal the amount of the un-reacted monomers which are leached out of the polymeric networks. The major cause of tissue inflammation as well as cytotoxicity is the monomers’ release[19]. It has been indicated that Degree of conversion (DC) and WSL are related, and low WSL could be the result of high DC[20]. This must be based on un-reacted monomers’ leachability in polymeric networks. Intermolecular hydrogen bond that is created via -NH- is weaker than the hydrogen bond created via -OH, due to the -OH group’s high cohesive energy density[20]. Thus, unreacted monomers can undergo a process of absorption to surrounding networks more firmly in Bis-GMA-based polymers in addition to being to leach out of polymers, which might lead to low WSL regarding the Bis-GMA-based polymers. Bis-GMA monomers result in more hydrophobic molecule; thus, the materials will have less susceptibility to liquid’s sorption as can be seen in Figure 2.

Since the polydimethacrylates can be considered as cross-linked dental polymers, and because of the polymer chains have cross-links between them, this will typically lead to considerable reduction in polymer’s solvent permeability since the reduce the capability related to polymer chain for swelling as well as reducing hole free volume[21]. Nevertheless, WS could be defined as needed impact as the composites’ hygroscopic expansion was indicated to the close marginal leakage gap because of the
shrinkage[22]. At the same time, a significant standard for the dental composites is the sufficient resistance to degradation via water and other solvents. It has been indicated that the dental composites are leaching only (0.02-0.05 percent) of their total mass to the aqueous solution through the first thirty days, this is the result of inorganic (Nanofillers).

3.1.3. Volumetric Shrinkage
The Volumetric Shrinkage (VS) values which are related to the specimens of the composites have been assessed on the basis of Archimedes principle. Uncured sample has been left to rest for one minute for the purpose of eliminating the impact of the slumping on measurements, then it has been exposed to 40s light curing, and the curing unit tip was placed at a distance of (1-2 millimeter) from specimen. The assessment has been implemented through the use of commercial Density Determination Kit of analytical balance Mettler Toledo X on the basis of ISO17304:2013 (E).

One of the main disadvantages, particularly in the dental composites is that their polymerization shrinkage could result in secondary caries and marginal gaps in restored teeth. Shrinkage is caused by the composites’ matrix-phase polymerization, also it is a main disadvantage in the dental resin-monomer. The polymerization of resin is accompanied by the volumetric shrinkage. As the polymerization proceeds, van der Waals distances have been modified to covalent bond distance which results in volumetric shrinkage. The shrinkage degree is represented through the number of the created covalent bonds that is defined as the polymerization reaction’s extent. Another reason for the volumetric shrinkage is that the molecular distances between polymer chains become smaller than the molecular distance between monomers[23].

Since the stresses generated from polymerization shrinkage cause defects of deboning at the tooth-restorative interface[24, 25], one of the main issues in the dental composites is to eliminate or decrease the polymerization shrinkage. In the case when the monomer in the proximity react to create covalent bonds, there will be a reduction in the distance between atoms groups, also the free volume will be decreased, that will lead to VS magnitude experienced through composites has been decided through its filler volume fraction as well as the conversion’s degree and composition of resin matrix. As shown in Figure 3. the composite with the Bis-GMA presented much smaller volumetric shrinkage. The shrinkage values which has been indicated for Bis-GMA (forty percent) and N,N MBAA (twenty percent) have been considerably more elevated than the shrinkage values related to the standard composites, that arein the range of 2 – 3 percent[26, 27]. Such difference is the result of the fact that in the hybrid composite, about sixty percent of volume has been occupied through filler particle. Even though that the inorganic content related to micro filled composites is approximately forty percent, their shrinkage values are considered to be comparable to hybrids, because of the existence of pre-polymerized composite particle, occasionally indicated as “organic fillers”, that will be rendering them in a way comparable to the hybrid composite with regard to actual volume fraction regarding the polymerizing resin. The shrinkage will also be affected via the diluents’ concentrations in resin matrix.

A new study indicated that high ratios of N,N MBAA/Bis-GMA in the experimental composite will lead to high contraction stress value because of the elevated VS, due to the improved conversions[28]. Due to the fact that they usually have low molecular weights in comparison to host monomers, the density of the polymerizable carbon double bonds will be increased via the “diluents” monomers that will result in more shrinkage. Also, the reaction environment’s mobility will increase because of the Tg as well as low viscosity of diluent, which will allow more effective conversions[29].

Previous studies showed that increasing light intensity resulted in more polymerization shrinkage for some composites, but not all materials[30, 31]. In our study, the effects of each curing mode on two composite resins were compared and no significant difference was observed. Each composite showed similar behavior in the face of modulation of the light intensity during photoactivation. Therefore, it must be put into perspective that this result is valid only for two resin composites in this study. Consequently, with regard to this study’s limitations, it might be indicated that the increase in the shrinkage of composites is related to the total energy of curing lights. Further research in this area is necessary in order to reveal the polymerization shrinkage of other composite resins.
3.1.4. Scanning Electron Microscopy

Monodispersed and spherical Nanoparticles were successfully synthesized. SEM was used to evaluate both the morphology of Nanoparticles and fillers composite surface following the fracture toughness test (SEM, LEO (Zeiss) 1540XB). Samples were prepared for SEM by placing a small amount of the sample powder on SEM tubes followed by coating with osmium in order to prevent charging of the samples and to reduce the Nanotube damage from the electron beam during imaging. Surface treatment has been of high importance to develop and efficient dental composites. In the case when the filler’s size is not more than thirty nm, agglomerations as well as aggregation of the Nano-particles will occur. Thus, interfacial adhesions between the filler and the polymer matrix will be improved via the agglomeration filler dispersion. The improvements in the mechanical and surface characteristics might be the result of these enhancements. With regard to the presented study, zirconium oxide as well as Nano-silica have been applied as filler, that has been mixed with various concentrations chosen of the monomer resin in addition to the additives for the dental restorative applications. Using zirconium oxide fillers and Nano-silica have been anticipated to have benefits and enhance the characteristics related to composite fabricated. Klapdhor and Moszner 14 have indicated that the mono-dispersed Nano-filler in
polymer matrix result in Nano-composite material of optimum mechanical characteristics, excellent process ability as well as high transparency.

Group A1. In this group was used (Bis-GMA, MA, AA) monomers at different concentration and used crosslink (N,N MBAA) at 20% after that 0.7 gm SiO2 and 0.5 gm ZnO were added. Figure 4 (a) shows that spherical shapes with different size range of 31.98 -83.76 nm of SiO2 in dental composites were obtained. The SEM micro-graph that is related to each one of the materials has been displayed in the Figure 4. (a&b) at 2 distinctive magnifications.

From Group A 2. In this group was used same monomers as in group A1 but the different from group A1 only in Nanofiller which was used 0.7 gm ZrO2 were added. Figure 5 (a) shows that spherical shapes with different size range of 34.59– 74.61 nm of zirconium oxide Nanoparticles composite with monomer were obtained. SEM micrograph of each material is shown in Figure 5 (a & b) at two different magnifications.

3.1.5. Thermal gravimetric analysis (TGA) study
Thermogravimetric Analysis determine the change in mass as temperature’s functions. It can be mainly applied to specify degradation temperature, material’s absorbed content, the level of inorganic as well
as the organic parts in the materials as well as residues of analysis solvent. It does use sensitive electronic balance through which a sample will be suspended in furnace, which is controlled through temperature programmer. Thermal characteristics of 4 samples of such polymers have been examined by TGA in Argon atmosphere at heating rate (10ºC per minute)[32-34]. With regard to this test, many values have been recognized including T$_i$, T$_{op}$, T$_f$, T$_{50%}$, Residue at 600 Celsius, and char yields at 400 Celsius as can be seen in (Table 2).

Temperatures of fifty percent weight loss of (DNC A1- DNC A3) of polymers have been between (382-390) ºC. The char results of (DNC A1)are 72%, (DNC A2)are 74% , (DNC A3)are 70.5% at 500 ºC in Argon atmosphere, indicating that they could satisfy the requirements of temperature resistance that may be utilized in a variety of applications. Weight residue of (DNC A1) are 69%, (DNC A2) are 70% , (DNC A3) are 68% , at 600 ºC.

Table 2: Some Thermal Stability Characteristics Curves Thermal Gravimetric Analysis (TGA) of polymers

| DNC  | T$_i$ (ºC) | T$_{op}$ (ºC) | T$_f$ (ºC) | T$_{50%}$ (ºC) | Residue at 600 ºC | Char % at 500 ºC |
|------|------------|---------------|------------|---------------|------------------|------------------|
| A1   | 321        | 352           | 430        | 385           | 72               | 69               |
| A2   | 304        | 348           | 427        | 390           | 74               | 70               |
| A3   | 298        | 335           | 433        | 382           | 70.5             | 68               |

DNC Dental Nano Composite
T$_{op}$ represents optimal temperature of decomposition.
T$_i$ represents the temperature of the initial decomposition.
T$_{50%}$ represents the temperature of 50% weight loss, which has been obtained from the TGA.
T$_f$ represents the final temperature of decomposition. The final degree of dissociation temperature.
Char% at 400 ºC represents the residual weight percentage at 500ºC in Argon by TGA.

3.1.6. Differential Scanning Calorimeter Analysis (DSC) Study

Differential Scanning Calorimetry, is a technique of thermal analysis that investigates how material’s heat capacity (Cp) is transformed by temperature. A known mass sample is heated or cooled and the variations in its heat capacity are observed as alterations in the heat flow. This allows to reveal transitions such as melts glass transitions (Tg), and the melting point (Tm) the crystallization degree (Tc) (20). The results of (DNC A1) polymer showed in figure (6) the value of the glass transition (Tg) of the mixture (104 ºC), indicating an increase in the flow of temperature and then increase the rate of absorption of the sample to the temperature until the melting point ( Tm) at (580 º C) if completely melted and then the rate of absorption of the sample to heat and by the curve was set the crystallization rate (Tc) of the mixture (126.8º C). The results of (DNC A2) showed in figure (6) the value of the glass transition (Tg) of the mixture (110º C), indicating an increase in the flow of temperature and then increase the rate of absorption of the sample to heat and by the curve was set the crystallization rate (Tc) of the mixture (120.4º C). The results of (DNC A3) polymer showed in figure (6) the value of the glass transition (Tg) of the mixture (112 º C), indicating an increase in the flow of temperature and then increase the rate of absorption of the sample to the temperature until the melting point ( Tm) at (582 º C) if completely melted and then the rate of absorption of the sample to heat and by the curve was set the crystallization rate (Tc) of the mixture (118.6 ºC)[35].

Table 3. Degree of Glass Transition, Melting Point and the Degree of Crystallization in the Differential Thermal Analysis

| DNC  | T$_g$ (ºC) | T$_m$ (ºC) | T$_c$ (ºC) |
|------|------------|------------|------------|
| A1   | 104        | 580        | 126.8      |
| A2   | 111        | 590        | 120.4      |
| A3   | 113        | 582        | 118.6      |

DNC Dental Nano Composite, Tg: Degree glass transition , Tm: Melting Point, Tc: Degree of crystallization
3.1.7. Flexural Strength and Elastic Modulus
The main objective in this study was to study the flexural strengths of the composite samples containing various mass fractions of Nanofillers (SiO$_2$, ZrO$_2$, and Hydroxyapatite) As shown in Figure 7, there is an initial increase in the flexural strength of the Nanoparticles filled composites as the filler content is increased from (0.66 to 8) wt.%. However, a decrease in strength values is observed at higher values of filler addition. Going back to the results obtained for the flexural strength, it should be reminded that, one of the major factors affecting the mechanical characteristics of composite samples is extent of interfacial interaction. In other words, poor interfacial interactions prevent a sufficient transfer of stress between components. In such cases, the addition of filler particles is expected to increase the number of weak links and therefore have a negative impact on strength. Therefore, we believe that the increase in the strength shown in Figure 7 is due to the reduced macromolecular mobility in the matrix and the drop in the strength. Values is most likely attributable to the overcoming effect of poor filler/matrix coherence at higher values of the filler content.

Spherical and evenly distributed micrometer size filler particles can be observed and a closer examination of this micrograph indicates that, as a result of a strong interfacial bond between the filler and resin, some filler particles have been effectively forced out of the matrix during the mechanical testing. The modulus of elasticity values were calculated from these data and are presented in Figure 7. As indicated in this table, except for the case of the sample containing 4.6 wt.% Nano fillers the increase in the content of the filler is accompanied with increased value of the elastic modulus. A possible explanation for the increased value of elasticity modulus is the more restricted motion of Bis-GMA matrix with an increase in the filler content[36]. Once again, at some critical value of the filler content the sample behavior is dominated by the poor bonding at the interface causing a decrease in modulus value. An exponential dependence of modulus of elasticity on filler content has already been reported in the literature[37]. Another point which can be concluded from the data is that there is no sign of plastic deformation prior to fracture in these samples.

These results show that all Nano particulate containing samples have significantly higher mean strength than those of the Nano filled composite samples 1. This implies an effective stress transfer as a result of good bonding between the Nano-sized particles and the matrix. It is also important to take into account that the filler fraction values were lower in the Nano-size filler containing composites compared to the Nanofilled composite samples prepared in this study. In summary, the data presented in this study on the mechanical properties of the Nano-sized filler containing samples, indicates that in spite of the lower weight fraction, the use of Nano-size Nanofillers particles resulted in a considerable enhancement in the mechanical properties of the dental restorative composite samples. Obviously, several factors are at play, but we believe that maybe the most important is the favorable adhesion between the Nano-size filler and the polymeric matrix. Incorporating of Nanofillers in dental composites enhanced the flexural strength by over 100%. The flexural strength enhancement may be a result of increased area of the surface of the
particles of the filler due to the reduced size of the particle that produces high energy of the surface at
interface of the filler-matrix. This results from the capability of those Nanoparticles in hindering the
propagation of cracks within the matrix of the dental composite based on the mechanism of the
strengthening, in addition to strong bonding between those particles and the resin matrix. Adding HA,
SiO$_2$, and zirconium oxide as Nano-particles leads in increasing both dental Nano composites’ flexural
modulus and strength. The cause of this kind of behavior is that high shear strength of the interface,
between matrix of the resin and the Nanoparticles of each of HA, SiO$_2$, and zirconium oxide associated
with the creation of physical cross-link bonding shielding or covering Nano-particles, which
successively prevent cracks from propagating inside the material, according to foregoing.
In addition to that, incorporating brittle Nano-particles in the matrix of the polymer enhances composite
stiffness with the restriction of polymer chain mobility in Nanocomposite. And sufficient Nano-particle
distribution, particularly at low Nano-particle additive percentages to composite materials, as it has been
performed in the presented study (Nano-particle content’s volumetric fraction in composites not higher
than18% ratio) which decreases Nano-particle agglomeration in the composite, which could result in
the reduction from location and the density of stresses are insufficient for breaking weak interface
interactions. Which is why, those small concentrations of the stress may be transferred easily from the
matrix to brittle Nano-particles, thereby permitting particles in contributing their property of the high
brittleness to composites therefore, it result in increasing both flexural modulus and strength.

3.1.8. Compressive Strength
The strength of Nanofillers reinforcement resin which is under compressive loading has been evaluated
with the approach which is used to test Nanofillers. The values have been stated in Figure 8 for
compressive strength values of synthetic polymer which has been reinforced by Nanofillers of a variety
of average size of particles. Some other materials, which are presently in general utilization, have been
illustrated for comparisons. Specimens which have been made by Nanofillers had were of high
compressive strengths. Which gives the confirmation of the existence of differences that are statistically
significant between all groups of samples. Moreover, the results of the compressive test have shown the
differences amongst samples SiO$_2$ (10-30nm)< ZrO$_2$ (20-30) nm< HA (60) nm. The testing of
compressive strength is utilized to assess mechanical characteristics of this type of material. Due to the
fact that the majority of the masticator loads belong to compressive forces class. There is a considerable
importance in evaluating the resin material durability in that conditions[38]. Advancements that have
been accomplished in the area of Nano-technology had a great influence on resins composition[39].
Many different types of composite were produced and presented according to the Nano-technology.
There is an importance of compressive strength measuring in vitro research which were characterized
as sufficient indicators for the simulation of functional forces which have loaded upon the restorative
materials that are under mastication[40-42]. Consequently, in the present work, Nano-composite resin’s
compressive strength has been projected. Composite resins that are Nano filled, combined with Nano
cluster formulations (that reduce filler particles’ interstitial spacing) to Nanosized particles. Which
presents higher loading of the filler, advanced physical characteristics, in comparison to these
complexes. The average sizes of filler particles range between (10nm and 30nm). Spherical shapes
include numerous benefits such as improvements in the filler load of the composites as well as increasing
fracture strengths due to the fact that mechanical stresses tend to be concentrated on filler particles’
angles and protrusions. The majority of the Nano-composites have filler particles that are spherically-
shaped that have improved filler load. In the present research, Nano-composites have higher
compressive strengths compared to compressive strengths of the other dental-composite. The present
research agrees in increased strength value of the Nano-composite resin. It has appeared that besides
greater sizes of filler particles in dental composite resins, the existence of SiO$_2$, hydro-apatite, and
zirconium fillers have a significant role in its enhanced strength. The existence of aromatic cycles in the
monomers such as Bisphenol di-methacrylate and Bis-GMA has been detected in dental composites
results in reducing cyclizing and increasing cross linking in the polymer and provides consecutive
enhancement in strength/durability and mechanical characteristics. None-the-less, in acrylate and
TEGDMA monomers particularly as a result of its high flexibility, there’s more chance of intermolecular cyclizing. In a way that Bis-GMA stiffness is a factor in improving compressive strength as well[43]. Esthetic properties of the Nano-composites are analogous to the esthetic characteristics of the natural teeth. Due to the fact that they are of a sufficient wear resistance they result in no enamel wear of analogous teeth. Their polymerization shrinkage is quite minor, which is why, they have less tension which results in decreasing of the over-sensitivity of post-op. there are filler particles in the Nano-composites, they enhance the strength of the matrix and produce higher toughness to fractures[44, 45]. Therefore, Nano-composites are of compressive strengths which are higher, which have been utilized in the present research where their higher strength may be clarified with their higher loadings of the filler. There have been numerous researches that reported the correlation between the volume fraction and the mechanical characteristics of the fillers[46-48].

4. Conclusions
This work has been focused on synthesizing a new Bis-GMA-based composite resin with Nanofillers (HA, SiO₂, and ZrO₂) for the use in the field of dentistry as restorative material. The filler that has been newly synthesized was a powder of white color, with carefully chosen particle sizes. The use of Nano-sized fillers particles has proven highly effective in the improvement of mechanical characteristics. Another benefit of the Nano-size reinforcement agents in comparison with the micro-sized particles has been the lower loading requirement. The enhanced mechanical characteristics which are shown by the complexes that include Nanoparticles is mostly a result of more efficient interaction of filler/polymer. A Nano-particle dispersion of higher efficiency, in combination with higher loadings could result in a
more enhanced complex dental restorative material. Additional researches are required for improving interactions between Nano-sized fillers and matrix phase and in addition to that, increasing Nano-filler particles’ loading capacity to the matrix of the polymer. In spite of the limitations of the present study, it might be concluded that dental Nanocomposites that are synthesized have several advantages, such as better water resistance and lower volumetric shrinkage. Even though the dental composite water solubility was small.

References:
[1] Albers H F 2002 Tooth-Colored Restoratives: Principles and Techniques (London: BC Decker INC. Hamilton)
[2] Summitt J B 2006 Fundamentals of Operative Dentistry: A Contemporary Approach (Chicago, USA: Quintessence Pub.)
[3] Kompozitn Š J 1988 materijali u stomatologiji. Zagreb: Grafički zavod Hrvatske;
[4] Puckett A D, Fitchie J G, Kirk P C and Gamblin J 2007 Direct composite restorative materials Dental clinics of North America 51 659-75; vii
[5] Mitra S B, Wu D and Holmes B N 2003 An application of nanotechnology in advanced dental materials Journal of the American Dental Association (1939) 134 1382-90
[6] Schmalz G and Arenholt-Bindslev D 2009 Biocompatibility of Dental Materials
[7] Oréfice R L, Discacciati J A C, Neves A D, Mansur H S and Jansen W C 2003 In situ evaluation of the polymerization kinetics and corresponding evolution of the mechanical properties of dental composites Polymeric Testing 22 77-81
[8] Pereira S G, Nunes T G and Kalachandra S 2002 Low viscosity dimethacrylate comonomer compositions [Bis-GMA and CH3Bis-GMA] for novel dental composites; analysis of the network by stray-field MRI, solid-state NMR and DSC & FTIR Biomaterials 23 3799-806
[9] Craig R 1997 Restorative Dental Materials (New York, USA: Mosby-Year Book)
[10] Moszner N and Salz U 2001 New developments of polymeric dental composites Progress in Polymer Science 26 535-76
[11] Sakaguchi R and Powers J 2012 Craig's Restorative Dental Materials: Elsevier Inc.)
[12] Barszczewska-Rybarek I M 2014 Characterization of urethane-dimethacrylate derivatives as alternative monomers for the restorative composite matrix Dental materials : official publication of the Academy of Dental Materials 30 1336-44
[13] Barszczewska-Rybarek I M 2009 Structure-property relationships in dimethacrylate networks based on Bis-GMA, UDMA and TEGDMA Dental materials : official publication of the Academy of Dental Materials 25 1082-9
[14] Sideridou I, Tserki V and Papanastasiou G 2002 Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins Biomaterials 23 1819-29
[15] Gajewski V E, Pfeifer C S, Froes-Salgado N R, Boaro L C and Braga R R 2012 Monomers used in resin composites: degree of conversion, mechanical properties and water sorption/solubility Brazilian dental journal 23 508-14
[16] Lemon M T, Jones M S and Stansbury J W 2007 Hydrogen bonding interactions in methacrylate monomers and polymers Journal of biomedical materials research. Part A 83 734-46
[17] Sideridou I, Tserki V and Papanastasiou G 2003 Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins Biomaterials 24 655-65
[18] Pfeifer C S, Shelton Z R, Braga R R, Windmoller D, Machado J C and Stansbury J W 2011 Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites European polymer journal 47 162-70
[19] Stansbury J W and Antonucci J M 1999 Dimethacrylate monomers with varied fluorine contents and distributions Dental materials : official publication of the Academy of Dental Materials 15 166-73
[20] Chang M C, Lin L D, Chuang F H, Chan C P, Wang T M, Lee J J, Jeng P Y, Tseng W Y, Lin H J and Jeng J H 2012 Carboxylesterase expression in human dental pulp cells: role in regulation of BisGMA-induced prostanoid production and cytotoxicity Acta biomaterialia 8 1380-7
[21] Kurata S and Yamazaki N 2011 Synthesis of dimethacryloxy ethyl-1,1,6,6-tetrahydro-perfluorohexamethylene-1,6-dicarbamate as dental base monomers and the mechanical properties of the copolymers of the monomer and methyl methacrylate Dental materials journal 30 103-8
[22] Giannini M, Di Francescanonio M, Pacheco R R, Cidreira Boaro L C and Braga R R 2014 Characterization of water sorption, solubility, and roughness of silorane- and methacrylate-based composite resins Operative dentistry 39 264-72
[23] Krevelen D W v 1990 Properties of Polymers (Amsterdam: Elsevier Inc.)
[24] Dickens S H and Cho B H 2005 Interpretation of bond failure through conversion and residual solvent measurements and Weibull analyses of flexural and microtensile bond strengths of bonding agents Dental materials : official publication of the Academy of Dental Materials 21 354-64
[25] Santos C, Clarke R L, Braden M, Guitian F and Davy K W 2002 Water absorption characteristics of dental composites incorporating hydroxyapatite filler Biomaterials 23 1897-904
[26] Labella R, Lambrechts P, Van Meerbeek B and Vanherle G 1999 Polymerization shrinkage and elasticity of flowable composites and filled adhesives Dental materials : official publication of the Academy of Dental Materials 15 128-37
[27] Stansbury J W 1990 Cyclopolymerizable monomers for use in dental resin composites Journal of dental research 69 844-8
[28] Feilzer A J and Dauvillier B S 2003 Effect of TEGDMA/BisGMA ratio on stress development and viscoelastic properties of experimental two-paste composites Journal of dental research 82 824-8
[29] Ferracane J L and Greener E H 1986 The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins Journal of biomedical materials research 20 121-31
[30] Braga R R, Hilton T J and Ferracane J L 2003 Contraction stress of flowable composite materials and their efficacy as stress-relieving layers Journal of the American Dental Association (1939) 134 721-8
[31] Calheiros F C, Sadek F T, Braga R R and Cardoso P E 2004 Polymerization contraction stress of low-shrinkage composites and its correlation with microleakage in class V restorations Journal of dentistry 32 407-12
[32] Tarasov A 2012 thermal analysis: methods,principles, applicason Lecture on Thermal analysis
[33] Dean S, Cantrell K, Martin J and Ro K 2010 Application of Thermogravimetric Analysis for the Proximate Analysis of Livestock Wastes Journal of Astm International 7
[34] Advarekara R V, Dasarwar S D and Khurana N S 2013 Synthesis of halogen free flame retardant and its application on polypropylene Indian Journal of Fibre & Textile Research 38 9-13
[35] Wunderlich B 1981 Thermal Analysis, text for an audio course. ATHAS, Advanced Thermal Analysis Alaboratory for Research and Instruction
[36] Asmussen E and Peutzfeldt A 1990 Mechanical properties of heat treated restorative resins for use in the inlay/onlay technique Scandinavian journal of dental research 98 564-7
[37] Willems G, Lambrechts P, Braem M, Celis J P and Vanherle G 1992 A classification of dental composites according to their morphological and mechanical characteristics Dental Materials 8 310-9
[38] Aghadazeh Mohandesi J, Rafiee M A, Barzegaran V and Shafiei F 2007 Compressive fatigue behavior of dental restorative composites Dental materials journal 26 827-37
[39] Ure D and Harris J 2003 Nanotechnology in dentistry: reduction to practice Dental update 30 10-5
[40] Anusavice K J 2003 Phillips Science of Dental Materials (Missouri, USA: Elsevier/Saunders)
[41] Ratanapridakul K, Leinfelder K F and Thomas J 1989 Effect of finishing on the in vivo wear rate of a posterior composite resin The Journal of the American Dental Association 118 333-5
[42] Salim F M 2019 Tribological and Mechanical Characteristics of Dental Fillings Nanocomposites Energy Procedia 157 512-21
[43] Elliott J E, Lovell L G and Bowman C N 2001 Primary cyclization in the polymerization of bis-GMA and TEGDMA: a modeling approach to understanding the cure of dental resins Dental materials : official publication of the Academy of Dental Materials 17 221-9
[44] Yap A U, Yap S H, Teo C K and Ng J J 2004 Comparison of surface finish of new aesthetic restorative materials Operative dentistry 29 100-4
[45] Chen M H, Chen C R, Hsu S H, Sun S P and Su W F 2006 Low shrinkage light curable nanocomposite for dental restorative material Dental materials : official publication of the Academy of Dental Materials 22 138-45
[46] Braem M, Finger W, Van Doren V E, Lambrechts P and Vanherle G 1989 Mechanical properties and filler fraction of dental composites Dental materials : official publication of the Academy of Dental Materials 5 346-8
[47] Chung K H and Greener E H 1990 Correlation between degree of conversion, filler concentration and mechanical properties of posterior composite resins Journal of oral rehabilitation 17 487-94
[48] Nuri Khaled A K 2012 Physical Properties of Dental Resin Nanocomposites. In: School of Dentistry, (Manchester, UK: The University of Manchester)