

Multilayered PMMA Dental Material Reinforced with Electrospun PVP/ZrO₂ Composite Nanofiber Fabrics with Enhanced Flexural Properties

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Abstract

Introduction: This study presents a new design of multilayered PMMA dental composite material combining electrospun continuous composite polyvinylpyrrolidone (PVP) nanofibers filled with zirconia (ZrO₂) nanoparticles and two-component self-cure PMMA dental resin. The aim is to improve the mechanical properties of dental PMMA material via the large surface area of electrospun nanofibers, the toughening effect of PVP and ZrO₂ nanofillers. **Methods:** First, PVP/ZrO₂ composite nanofibers with different ZrO₂ contents of 5%, 10% and 20% (wt. % of PVP) were prepared by electrospinning. Then, multilayered samples containing alternating PMMA resin and electrospun composite nanofiber mats with different ZrO₂ contents were manufactured by lay-up process. Samples containing single and double layers of nanofiber mats were prepared and cured in a water bath dental acrylic curing device in order to prepare composites without any void. **Results:** FTIR and SEM results reveal that PVP enables good interfacial interactions and compatibility between the nanofibers and PMMA matrix. The mechanical properties are improved as an increase of the flexural strength up to 83% and 67% is observed for PMMA/PVP/ZrO₂-10s and PMMA/PVP/ZrO₂-20d samples, respectively. The presence of PVP nanofiber layers significantly improves the flexural toughness, especially for samples reinforced with a single layer of nanofibers where improvements up to 169% and 153% are observed for PMMA/PVP/ZrO₂-5s and PMMA/PVP/ZrO₂-10s composite samples respectively. The micro-hardness is also higher for composite samples compared to neat PMMA dental material. **Conclusion:** The overall results clearly depict a noticeable enhancement of the mechanical properties,

especially the flexural toughness of PMMA dental material.

Keywords: Dental Composite, PMMA, Electrospinning, PVP/ZrO₂ Composite Nanofibers, Flexural Properties

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Introduction

Dental prostheses must have sufficient physical and mechanical properties as they contribute to the patients declining functional needs. The denture base must be strong enough to allow the prosthesis to withstand functional and parafunctional masticatory forces (1). Polymethyl methacrylate (PMMA) is an acrylic polymer widely used in prosthodontics or restorative dentistry. This material is highly favored due to its low density, cost-effectiveness, ease of manipulation, desirable aesthetics and tailorabile physical and mechanical properties. Although some concerns exist about the use of PMMA, this material is still advantageous for many applications in dentistry or restorative dentistry (2). The incorporation of reinforcements into polymeric prosthetic base materials is a way to strengthen them. This reinforcement can be achieved through different methods. Several studies have investigated the use of different types of fibers, such as carbon, polyethylene, polyamide and particularly glass fibers, due to their biocompatibility and mechanical properties (3,4). Fiber reinforcement of PMMA acrylic resin has been reported to improve the flexural and impact strength as well as the

fatigue resistance of the resin (5-9). Although carbon fibers have been extensively investigated by researchers, their clinical use is still not widely accepted due to the aesthetic concerns caused by the black color of these fibers (10,11). The literature also indicates that incorporating inorganic microscale or nanoscale particulate fillers in PMMA matrix enhances its mechanical properties (2,12).

It is well known that due to their large surface area, nanoscale reinforcements enable the design of nanocomposites with superior mechanical and physical properties. Electrospun polymer nanofibers are emerging materials and their use as reinforcement filler in polymer matrix composites is gaining increasing attention. These continuous nanofibers are particularly interesting due to their processing ease. However, only a few studies exist in the literature on the use of continuous electrospun polymer nanofibers as reinforcement in PMMA dental material. Elmadani et al. reinforced PMMA dental resin with zirconia (ZrO_2) nanoparticle powder and electrospun polystyrene nanofibers (13) in order to improve the mechanical properties of PMMA dental material. Although acceptable interactions between ZrO_2 nanoparticles and PMMA matrix were observed, the authors also noticed poor interfacial interactions between PS nanofibers and PMMA resin inducing a phase separation between the two polymers. According to the cited authors, the optimization of ZrO_2 nanoparticles content is necessary as these particles migrate into the voids between PS nanofibers and PMMA matrix which decreases the hardness and T_g values of the dental composites. The use of nonwoven fabrics of electrospun continuous PAN-PMMA core-shell nanofibers as reinforcement in PMMA dental material was also explored (14,15). The results showed that the PMMA chains forming the shell of the electrospun nanofibers interpenetrate and entangle with the crosslinked PMMA chains of the matrix and therefore, an in-situ semi-interpenetrating polymer network (semi-IPN) is formed. Hence, the interactions between the PMMA matrix and electrospun nanofibers are improved which is reflected on the mechanical properties as an enhancement.

Mechanical properties and especially toughness are the main features of dental composites that are in need of improvement. Studies showed that polyvinylpyrrolidone (PVP) can enhance these properties in particulate filled composites by favoring filler-matrix interactions (16,17). Therefore, the aim of this study is to propose a PMMA dental composite material with improved flexural properties and toughness via the use of ZrO_2 filler and electrospun PVP nanofibers. In order to address this objective, multilayered dental materials comprising layers of electrospun continuous nonwoven PVP/ ZrO_2

composite nanofiber mats and PMMA dental resin were designed. Characteristics such as the morphology, the interfacial interactions and particularly the flexural mechanical properties were characterized.

Materials and Methods

2.1. Materials

A two-component commercial self-cure PMMA dental material (Integra, Bgd, Turkey) composed of PMMA powder and methyl methacrylate (MMA) liquid was used as matrix. Polyvinylpyrrolidone (K85-95) was purchased from Acros Organics. Ethanol (96% purity) was supplied from Aytaş, Turkey. Zirconia ZrO_2 (50 nm) powder was provided by Zirkings Huge Dental, China.

2.2. Fabrication of PVP/ ZrO_2 composite nanofiber mats

PVP solutions in ethanol of 7% (w/w) and with ZrO_2 contents of 5%, 10% and 20% (wt.% of PVP) were prepared. For this purpose, PVP powder was dissolved in ethanol under constant stirring at ambient temperature until complete dissolution. Then, ZrO_2 particles were dispersed in PVP solutions using an ultrasonic homogenizer (MSK-USP-12N).

PVP and PVP/ ZrO_2 solutions were electrospun using an in-house electrospinning device at a high voltage of 17.5 kV, a tip-to-collector distance of 15 cm and a flow rate of 1.25 mL/h. Nonwoven nanofibers were gathered on a plate aluminum collector.

2.3. Fabrication of multilayered dental composites

A stainless-steel mold was used to prepare cylindrical multilayered dental composite materials specimens of 10 mm diameter and 2 mm height as schematically represented in Figure 1. For this purpose, cylindrical nanofiber mat pieces of 10 mm diameter were delicately cut. The PMMA matrix was prepared by vigorously mixing the two components with a powder: liquid ratio of 24g: 10mL during 1 min. Then, nanofiber pieces were laminated into self-cure dental PMMA resin, layer by layer. Samples with PVP nanofiber mat/fabric and PVP/ ZrO_2 composite nanofiber fabrics of different contents of ZrO_2 (5%, 10% and 20% (wt. % of PVP)) were prepared. The multilayered composites were cured in a water bath dental acrylic curing device (Ekstromat) at 55°C for 10 min under a pressure of 20 psi. This process allows the preparation of multilayered PMMA composites without any void. The PVP/ ZrO_2 composite nanofibers are totally immersed into the PMMA resin. In order to characterize the flexural properties of multilayered dental materials, bar-specimens of 2x2x25 mm were also prepared, as recommended by the American Dental Association (ADA) specifications No.

27, using a stainless-steel mold. The same lamination procedure used for the fabrication of cylindrical samples was applied to prepare multilayered bar-shaped specimens using nanofiber mat pieces of 2x2x25 mm. For all compositions, specimens with single and double layers of nonwoven nanofiber mats were prepared. Samples reinforced with a single PVP or PVP/ZrO₂

composite nanofiber layer are referred as PMMA/PVPs, PMMA/PVP/ZrO₂-5s, PMMA/PVP/ZrO₂-10s, PMMA/PVP/ZrO₂-20s and those reinforced with double layer of PVP or PVP/ZrO₂ composite nanofiber as PMMA/PVPd, PMMA/PVP/ZrO₂-5d, PMMA/PVP/ZrO₂-10d, PMMA/PVP/ZrO₂-20d.

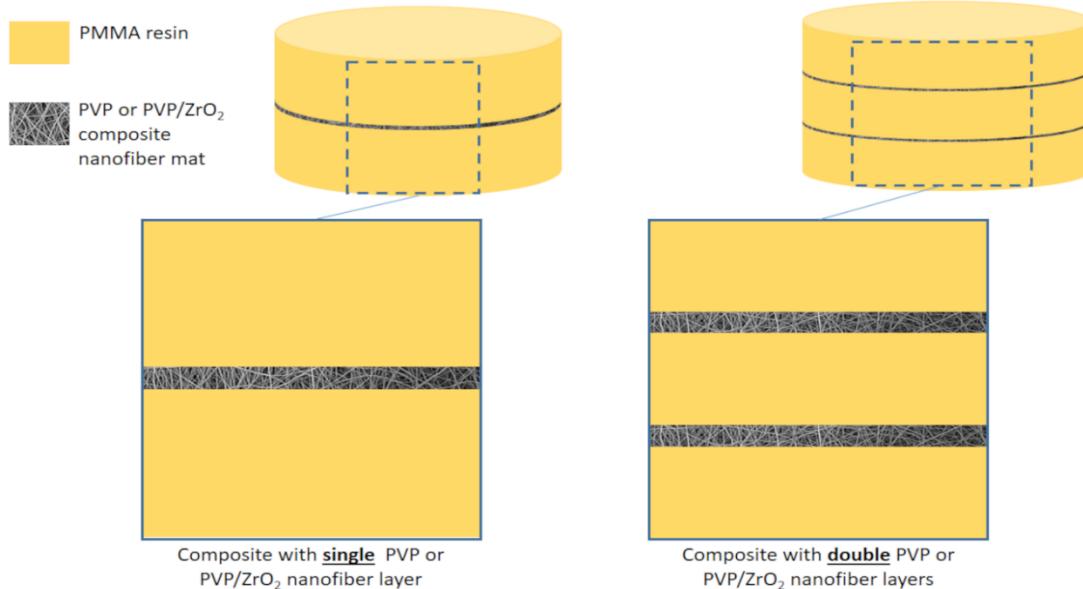


Figure 1: Schematic representation of the composite structures designed in this study.

2.4. Characterization

The morphology of the nanofibers and fractured multilayered composites were characterized by scanning electron microscopy (HITACHI FlexSEM 1000, Tokyo, Japan) at 15 kV. The diameters of the electrospun nanofibers were determined using IMAGE J software (v. 1.52i, National Institute of Health, USA) from 100 nanofibers as described by Maleki et al. (18).

The chemical structure of the composites was investigated by Fourier Transform Infra-Red (FTIR) spectroscopy using a ThermoFisher Nicolet IS50 (Waltham, Massachusetts, USA) device equipped with an Attenuated Total Reflection (ATR) element within a range of 4000-400 cm⁻¹.

Three-point bending measurements were realized on rectangular shaped composite samples having dimensions of 2x2x25mm using a Lloyd LRX (West

Sussex, United Kingdom) universal testing machine with a crosshead speed of 5 mm/min as recommended by ADA specification No. 27. Eight replicates were used for each sample.

The micro-hardness of the dental materials prepared was determined using a Shimadzu HMV-G (Kyoto, Japan) micro-hardness tester equipped with a Vickers diamond indenter. Indentations were made using a 50g load with 10s dwell time. Seven replicates were prepared for each sample.

Results

3.1. Morphology and diameter of electrospun PVP/ZrO₂ composite nanofibers

SEM micrographs and diameter distributions of the PVP/ZrO₂ composite nanofibers are presented in Figure 2 and mean diameters are gathered in Table I.

Table I. Diameters of the electrospun PVP and PVP/ZrO₂ composite nanofibers.

Nanofiber mats	Nanofibers mean diameter (nm)
PVP	175 ± 28
PVP/ZrO ₂ -5	160 ± 39
PVP/ZrO ₂ -10	184 ± 35
PVP/ZrO ₂ -20	190 ± 30

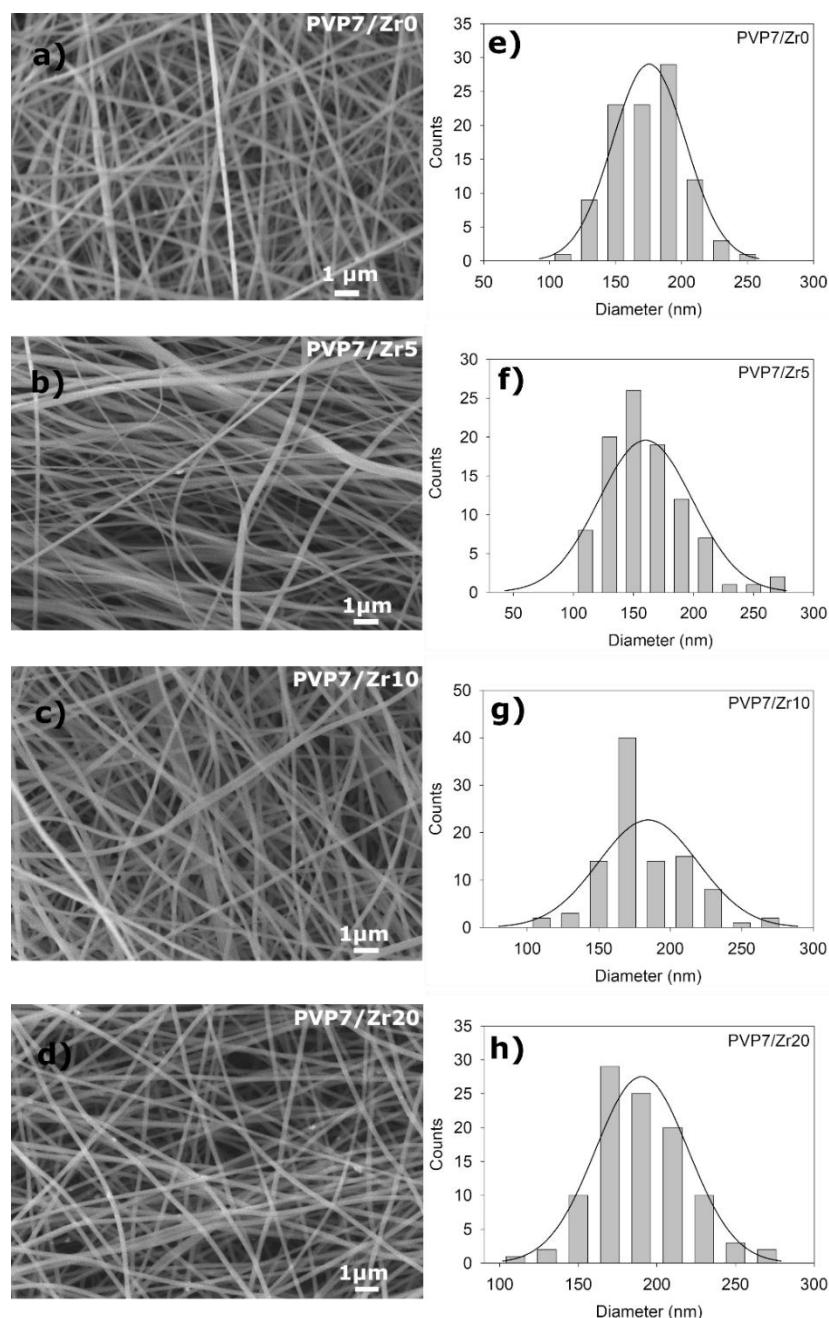


Figure 2: SEM micrographs of the electrospun PVP and PVP/ZrO₂ composite nanofibers with a) 0%, b) 5%, c) 10% and d) 20% of ZrO₂ and the corresponding nanofiber diameter distributions from e) to h)

FTIR spectra of PVP, PMMA and composite samples are presented on Figure 3.

3.2. Fourier-Transform Infrared spectroscopy

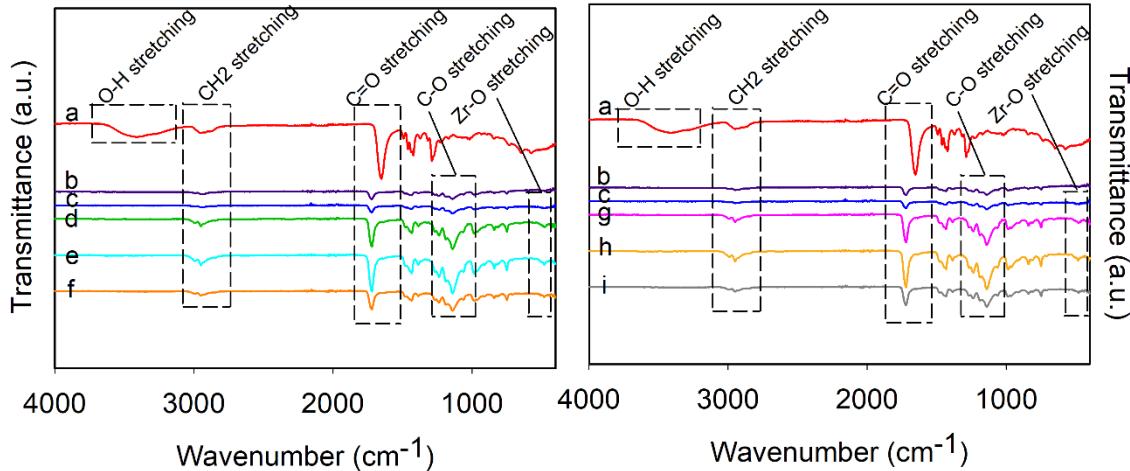


Figure 3: FTIR spectra of a) PVP, b) PMMA resin and multilayered composites c) PMMA/PVP, d) PMMA/PVP/ZrO₂/5-s, e) PMMA/PVP/ZrO₂/10-s, f) PMMA/PVP/ZrO₂/20-s, g) PMMA/PVP/ZrO₂/5-d, h) PMMA/PVP/ZrO₂/10-d, f) PMMA/PVP/ZrO₂/20-d.

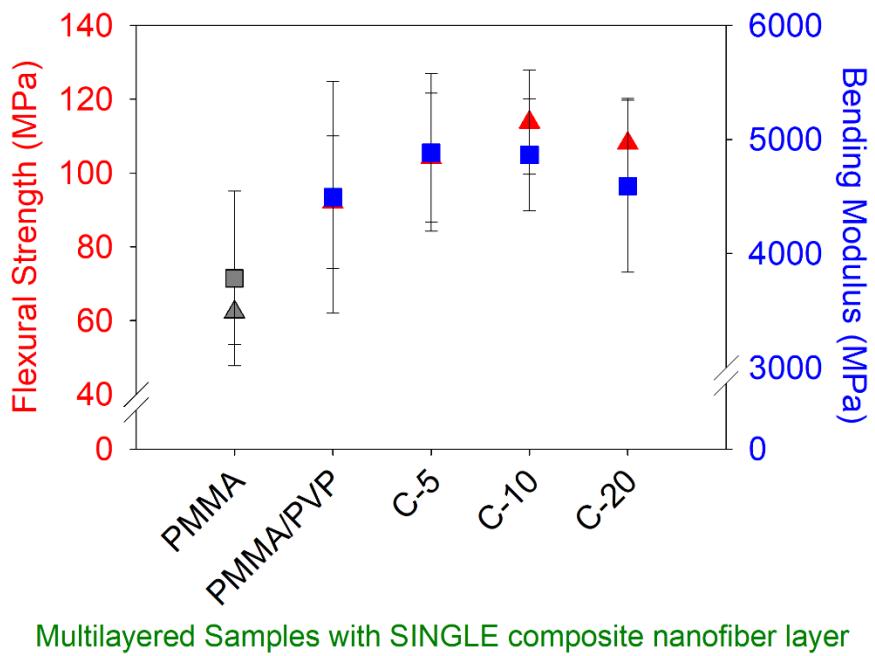
3.3. Three-point bending

The flexural properties of the samples were characterized by three-point bending measurements. The flexural strength of the samples was calculated using Equation 1 (19).

$$\sigma = \frac{3FL}{2bh^2} \quad \text{Equation 1}$$

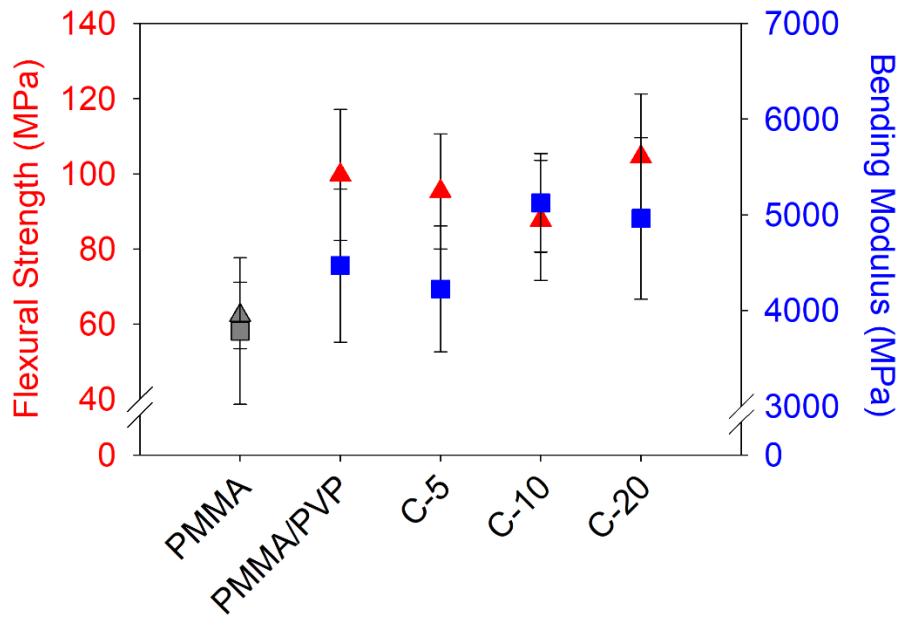
where F is the applied load, L is the span, b and h are the width and the thickness of the samples.

The flexural strength and bending modulus of samples with a single composite nanofiber layer and of those with double PVP/ZrO₂ composite nanofiber layers are given in Figures 4 and 5, respectively. The flexural toughness of the samples was also evaluated and the results are presented in Figure 6.



Multilayered Samples with SINGLE composite nanofiber layer

Figure 4: Evolution of flexural strength (triangles) and bending modulus (squares) of PMMA resin and multilayered dental composites with a single layer of PVP or PVP/ZrO₂ composite nanofibers: PMMA/PVP, PMMA/PVP/ZrO₂-5 (C-5), PMMA/PVP/ZrO₂-10 (C-10), PMMA/PVP/ZrO₂-20 (C-20).



Multilayered Samples with DOUBLE composite nanofiber layers

Figure 5: Evolution of flexural strength (triangles) and bending modulus (squares) of PMMA resin and multilayered dental composites with a single layer of PVP or PVP/ZrO₂ composite nanofibers: PMMA/PVP, PMMA/PVP/ZrO₂-5 (C-5), PMMA/PVP/ZrO₂-10 (C-10), PMMA/PVP/ZrO₂-20 (C-20).

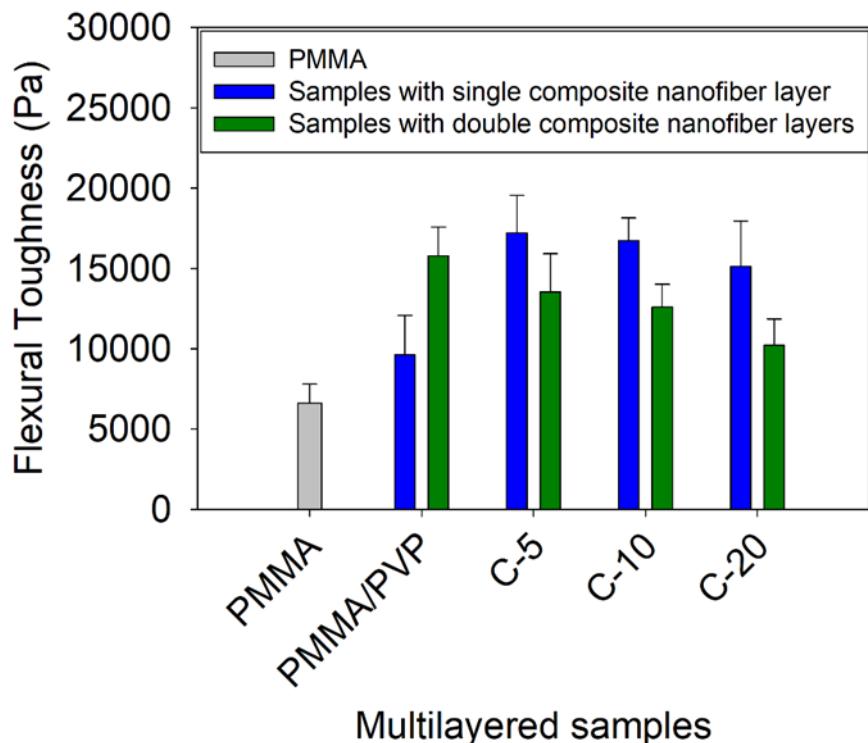


Figure 6: Evolution of the flexural toughness of PMMA resin and multilayered dental composites: PMMA/PVP, PMMA/PVP/ZrO₂-5 (C-5), PMMA/PVP/ZrO₂-10 (C-10), PMMA/PVP/ZrO₂-20 (C-20) with a single or double layers of nanofibers.

The results reveal that the flexural strength (Figures 4 and 5) is higher than unfilled PMMA resin for all composite samples. In the case of samples reinforced with a single layer of PVP or PVP/ZrO₂ composite nanofibers (Figure 4), an improvement of 48%, 67%, 83% and 73% was observed for PMMA/PVPs, PMMA/PVP/ZrO₂-5s, PMMA/PVP/ZrO₂-10s, PMMA/PVP/ZrO₂-20s composite sample, respectively. Concerning the samples reinforced with double layers of PVP or PVP/ZrO₂ composite nanofibers (Figure 5), improvements of 60%, 53%, 41% and 67% were obtained for PMMA/PVPd, PMMA/PVP/ZrO₂-5d, PMMA/PVP/ZrO₂-10d, and PMMA/PVP/ZrO₂-20d composite samples, respectively.

The bending moduli of the samples are also presented in Figures 4 and 5. An increase of the bending modulus (compared to PMMA resin) of 19%, 29%, 29% and 21% was obtained for PMMA/PVPs, PMMA/PVP/ZrO₂-5s, PMMA/PVP/ZrO₂-10s, PMMA/PVP/ZrO₂-20s samples reinforced with a single layer of PVP or PVP/ZrO₂ composite nanofibers (Figure 4), respectively, whereas 18%, 12%, 35% and 31% of increase are observed for PMMA/PVPd, PMMA/PVP/ZrO₂-5d, PMMA/PVP/ZrO₂-10d, PMMA/PVP/ZrO₂-20d samples

reinforced with double layers of PVP or PVP/ZrO₂ composite nanofibers, respectively (Figure 5).

The flexural toughness corresponds to the area under the stress-strain curve or under the load-deformation curve (20-22). Therefore, the area under the stress-strain curve was calculated for each sample and the results are presented in Figure 6. A significant improvement of the toughness of PMMA dental material is observed.

3.4. Micro-hardness

The micro-hardness of the samples was determined by measuring the two diagonal lengths of each indentation which were converted into micro-hardness values (VH) using Equation 2.

$$HV = 1.854 \frac{P}{d^2} \quad \text{Equation 2}$$

where HV is the micro-hardness in kg/mm², P is the load in kgf and d is the average length of the diagonals in mm.

For each sample, the average value of the seven replicate measurements is reported in Figure 7. The overall trend is upward for all samples containing either one layer or two layers of PVP or PVP/ZrO₂ composite nanofiber mats as their micro-hardness is higher than PMMA dental material.

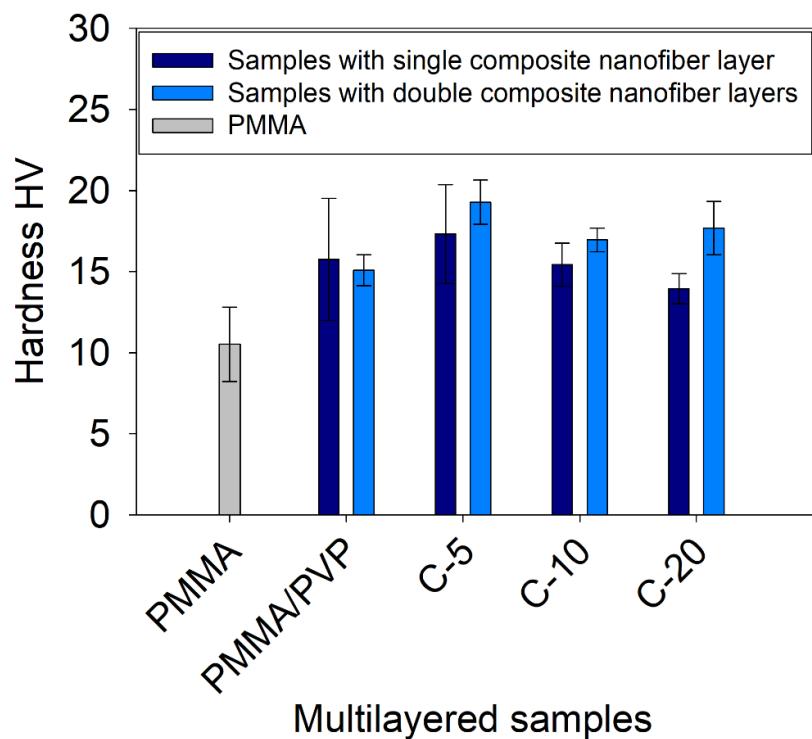


Figure 7: Evolution of the micro-hardness of PMMA dental material and multilayered dental composites: PMMA/PVP, PMMA/PVP/ZrO₂-5 (C-5), PMMA/PVP/ZrO₂-10 (C-10), PMMA/PVP/ZrO₂-20 (C-20) with a single or double layers of nanofibers.

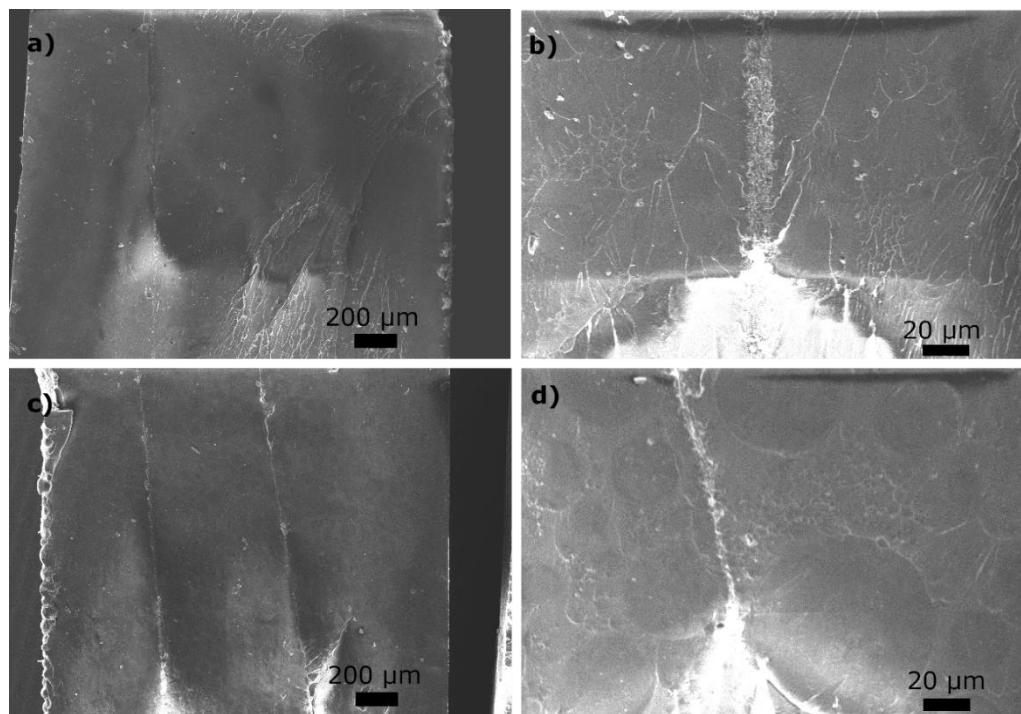


Figure 8: SEM micrographs of fractured composites a) PMMA/PVP/ZrO₂-10-d sample, b) close up image of PMMA/PVP/ZrO₂-10-d sample, c) PMMA/PVP/ZrO₂-20-d and d) close up image of PMMA/PVP/ZrO₂-20-d sample.

Discussion

4.1. Effect of ZrO₂ filler on the morphology and diameter of PVP/ZrO₂ composite nanofibers

According to the micrographs shown in Figure 2 and the results presented in Table I, the diameter of the nanofibers increases with increasing ZrO₂ content. As expected, all the composite mats are composed of homogeneous cylindrical continuous nanofibers. A broader diameter distribution is observed in the case of PVP/ZrO₂ composite nanofibers. These results are similar to those observed by Thakare et al. (23) with ZrO₂ reinforced polycaprolactone (PCL) nanofibers. The authors obtained uniform, highly porous and smooth nanofibers even with increasing ZrO₂ content.

4.2. FTIR analysis: intermolecular interactions

The FTIR spectrum of PVP presents a large peak at 3424 cm⁻¹ which is ascribed to the presence of (O-H) stretching (24,25). An asymmetric stretching of CH₂ is shown by the peak at 2950 cm⁻¹. The peak at 1652 cm⁻¹ indicates a (C-O) stretching. The peak at 1423 cm⁻¹ corresponds to the C-H bending and CH₂ wagging is characterized by the peak at 1286 cm⁻¹. The peak at 1649 cm⁻¹ is attributed to the carbonyl stretching (C=O) and the peak at 1494 cm⁻¹ characterizes the (C-N) ring vibrations (26). The FTIR spectrum of PMMA presents the characteristic functional groups of this polymer. The ester carbonyl group (C=O) stretching vibration appears as a sharp peak at 1730 cm⁻¹. The ester bond (C-O) stretching is observed via a broad peak within the range of 1300-1000 cm⁻¹. Moreover, the peaks between 950 and 650 cm⁻¹ are attributed to the (C-H) bending (27). For both PMMA and PVP, the peaks between 2800 and 3000 cm⁻¹ are attributed to symmetric and asymmetric stretching of CH₂ groups. The shifting of these peak to higher wavenumbers in multilayered dental composites may show strong interactions between PVP and PMMA matrix (26). The FTIR spectra of PMMA and composite samples are quite similar except within the range of 500-700 cm⁻¹. Especially, the broad peak between 430 and 599 cm⁻¹ appears for PMMA/PVP/ZrO₂ composite samples (28). This peak is attributed to the stretching of (Zr-O) bond and shows that PVP/ZrO₂ composite nanofibers are well integrated into the PMMA matrix (23, 28). Moreover, the reduction of the relative intensity of the characteristic peak of PVP at 1286 cm⁻¹ in the multilayered samples may be due to strong interactions between the backbone of PVP and PMMA chains (26).

4.3. Interfacial morphology and interfaces between PMMA matrix and PVP/ZrO₂ composite nanofiber mats

In order to investigate the interfaces between PVP/ZrO₂ composite nanofiber mats and PMMA resin, the fractured samples were observed by Scanning Electron Microscopy. For clarity, only the SEM micrographs of samples PMMA/PVP/ZrO₂-10-d and PMMA/PVP/ZrO₂-20-d are presented in Figure 8. No voids/interspaces between PMMA matrix and composite nanofibers are observed. Therefore, PVP/ZrO₂ mats are perfectly impregnated by PMMA resin indicating a good adhesion between the nanofiber mat and the matrix (29,30). These results are in correlation with FTIR analysis. The PMMA dental material used in the study is a conventional powder-liquid system. The liquid component is actually an adhesive monomer, MMA, which contains both hydrophobic and hydrophilic groups, specifically designed in order to enhance the bonding strength of the material (12). This property is important because as PVP is highly hydrophilic, it can undergo strong interactions with PMMA dental material which may explain the good adhesion and compatibility between PVP nanofibers and PMMA matrix. These results are actually in correlation with the related literature (26).

4.4. Mechanical properties of layered dental composites

4.4.1. Flexural properties

According to Figures 4 and 5, the flexural strength increases until a ZrO₂ filler content of 10% for samples with a single composite nanofiber layer. No trend emerges for double composite nanofiber layer containing samples although their flexural strength is higher than the PMMA resin. Uyar et al. studied the effect of oriented and non-oriented PVA nanofibers on the properties of PMMA resin (20). They observed that the presence of PVA nanofibers induces an improvement of the flexural strength. According to the authors, although the flexural strength increases in all cases, this evolution is valid until a critical fiber loading of 0.25% after which a slight decrease occurs. These results seem in correlation with our study as the flexural strength is improved for all composite samples compared to neat PMMA resin. It is worthwhile to notice that in case of PMMA/PVP samples filled with one or two layers of PVP nanofibers, the flexural strength is higher for double layer filled samples. Moreover, as anticipated, the presence of the inorganic filler ZrO₂ improves the flexural strength. However, contrary to expectations, for all samples filled with PVP/ZrO₂ composite nanofibers, the flexural strength is lower for samples containing a double layer of PVP/ZrO₂ composite nanofibers compared to those reinforced with a single layer. According to the literature, values of satisfactory flexural strength are reported as 92.84 ± 4.73, 84.40 ± 1.68, and 109.63 ± 5.31 MPa for heat-cured,

cold-cured and microwave-cured PMMA dental materials, respectively (31,32). Therefore, the composites designed in this study satisfy this criterion.

Concerning the bending modulus of the samples, it actually rises in the presence of electrospun PVP or PVP/ZrO₂ composite nanofiber layers (compared to PMMA resin) for all composites and no real trend emerges.

The results presented in Figure 6 show a significant improvement of the toughness of PMMA dental material and the conclusion is twofold. In the case of PMMA/PVP multilayered samples, the toughness increases up to 139% (compared to PMMA) for the sample containing two layers of PVP nanofibers whereas only 45% of increase is observed for the sample containing one layer of PVP nanofibers. This evolution is in correlation with the literature. It is well known that PVP helps to improve the toughness of particulate filled polymer composites (16,17). In the case of multilayered samples reinforced with ZrO₂ filled PVP nanofibers, an improvement of the toughness of 160%, 153% and 129% were obtained for PMMA/PVP/ZrO₂-5s, PMMA/PVP/ZrO₂-10s, PMMA/PVP/ZrO₂-20s samples, respectively. On the other hand, the toughness is improved of 105%, 91% and 54% for PMMA/PVP/ZrO₂-5d, PMMA/PVP/ZrO₂-10d, PMMA/PVP/ZrO₂-20d samples, respectively. Although the flexural toughness is improved for all cases, it decreases with increasing ZrO₂ content in reinforced PVP nanofibers.

4.4.2. Micro-hardness

As mentioned above, the overall trend is upward for all samples containing either one layer or two layers of PVP or PVP/ZrO₂ composite nanofiber mats as their micro-hardness is higher than PMMA dental material. These results are in correlation with the conclusions of Alqahtani et al. (2) who observed an increase of Vickers hardness in PMMA dental materials reinforced with ZrO₂ nanoparticles. Despite this general improvement of the micro-hardness, no real trend emerges for the composite samples.

Conclusion

Multilayered PMMA dental composites reinforced with single or double layers of electrospun PVP or PVP/ZrO₂ composite nanofibers were prepared. FTIR and SEM results show good interfacial interactions and compatibility of PVP or PVP/ZrO₂ nanofibers into PMMA matrix. Noticeable improvements of mechanical properties were also observed. The flexural strength was improved for either single or double layer filled PMMA samples. An increase up to 83% and 67% was observed

for PMMA/PVP/ZrO₂-10s and PMMA/PVP/ZrO₂-20d samples, respectively. Moreover, the presence of polymer nanofiber layers significantly improved the flexural toughness, especially for samples filled with a single layer of nanofibers where improvements up to 169% and 153% were observed for PMMA/PVP/ZrO₂-5s and PMMA/PVP/ZrO₂-10s composite samples, respectively. Then, the micro-hardness was also higher for the composite samples compared to unfilled PMMA dental material. These overall results clearly depict a noticeable enhancement of the mechanical properties, especially the flexural toughness of PMMA dental material due to the presence of electrospun composite polymer nanofiber layers.

Conflicting Interests:

The Authors declare that there is no conflict of interest.

Acknowledgment:

Non

References

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