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## Amorphous calcium phosphate composites with improved mechanical properties

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### Abstract

Hybridized zirconium amorphous calcium phosphate (ACP)-filled methacrylate composites make good calcium and phosphate releasing materials for anti-demineralizing/remineralizing applications with low mechanical demands. The objective of this study was to assess the effect of the particle size of the filler on the mechanical properties of these composites. Photo-curable resins were formulated from ethoxylated bisphenol A dimethacrylate, triethylene glycol dimethacrylate, 2-hydroxyethyl methacrylate and methacryloxyethyl phthalate. Camphorquinone and ethyl-4-N,N-dimethylaminobenzoate were utilized as components of the photoinitiator system. After 2 h of mechanical milling in isopropanol, an approximate 64 % reduction in the median particle diameter was observed [27.48  $\mu\text{m}$  vs. 9.98  $\mu\text{m}$ ] for unmilled and milled *wet* ACP, respectively. Dry ACP showed a 43 % reduction in particle size from pre- to post-milling. As well as dry composites, those that had been immersed in aqueous media were evaluated for their Young's Modulus, water sorption, biaxial tensile, three-point flexural and diametral tensile strength. Mechanically milling the filler increased the volume of fine particles in the composite specimens, resulting in a more homogeneous intra-composite distribution of ACP and a reduction in voids. In turn, less water diffused into the milled composites upon aqueous exposure, and they showed a marked improvement in biaxial flexure strength and a moderate improvement in flexural strength over composites with unmilled ACP. The demonstrated improvement in the mechanical stability of milled Zr-ACP composites may help in extending their dental applicability.

### INTRODUCTION

Recently developed amorphous calcium phosphate (ACP)-filled polymeric dental composites based on photocurable dental resins are capable of releasing significant amounts of calcium and phosphate ions in a sustained manner in aqueous milieu [1–5]. These bioactive composites are potentially effective anti-demineralizing/remineralizing agents for the preservation and repair of teeth with foreseeable applications as dental restorative composites, adhesives, cements, protective liners and bases, pit and fissure sealants and orthodontic bracket cements. Other potential applications include osteoconductive bone cements and bone fixation devices. Compared to the more commonly used, but biologically inactive glass fillers, the more

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hydrophilic and biodegradable ACP has deficiencies as a reinforcing filler. Especially when compared to silanized glass-reinforcing composites, ACP composites exhibit inferior mechanical properties, durability and water sorption characteristics. To overcome these drawbacks, we have focused on improving the interfacial state existing between the ACP filler and polymer matrix through better control of three factors: the particle size distribution and surface properties of ACP fillers, and the chemical composition of the resin. How the filler particle size affects the properties of ACP composites is the primary focus of this study.

So far, our attempts to improve the mechanical performance of bioactive ACP composites via silanization and surface modification of the ACP during its synthesis have shown only a limited success [3]. It has been demonstrated that the uncontrolled aggregation of ACP particles is the dominant factor that controls the filler/matrix interface [4]. Coupled with the hydrophilic character of the filler, this leads to the relative high water sorption of the composites. A moderate success was achieved by resin tuning with regard to ion release (remineralizing potential) [5] but no substantial improvements have been achieved with respect to the mechanical stability of these composites upon prolonged aqueous immersion.

In this paper we report on the effect of mechanical milling on the particle size distribution of the ACP filler. The mechanical properties and water sorption behavior of milled ACP composites are compared with the same properties of composites utilizing the identical polymer matrix and the unmilled (as-synthesized) ACP.

## MATERIALS AND METHODS

### Synthesis of the Filler

Zirconia (Zr)-ACP precipitated instantaneously at 23 °C upon rapidly mixing equal volumes of a 800 mmol/L  $\text{Ca}(\text{NO}_3)_2$  solution, a 536 mmol/L  $\text{Na}_2\text{HPO}_4$  solution that contained a molar fraction of 2 %  $\text{Na}_4\text{P}_2\text{O}_7$  as a stabilizing component for ACP, and an appropriate volume of a 250 mmol/L  $\text{ZrOCl}_2$  solution (mole fraction of 10 %  $\text{ZrOCl}_2$  based on Ca reactant). The reaction pH varied between 8.6 and 9.0. The suspension was filtered, the solid phase subsequently washed with ice-cold ammoniated water and then acetone, and finally lyophilized.

### Mechanical Milling

Approximately 23 g of Zr-ACP solid were mixed with 550 g of very high density  $\text{ZrO}_2$  balls (3 mm in diameter; Glen Mills Inc., Clifton, NJ, USA) and 150 mL isopropanol (analytical grade; J.T. Baker, Phillipsburg, NJ, USA) and then sealed in a grinding jar. The jar (total mass = 7.4 kg) was clamped into the latching brackets and then counterbalanced on the mill (planetary ball mill PM100; Retch, Inc., Newtown, PA, USA). The milling was performed at 42 rad/s for 2 h with rotation reversed every 15 min. Milled Zr-ACP solid was removed from the  $\text{ZrO}_2$  balls by sieving. Isopropanol was then evaporated in a vacuum oven (Squaroid Labline vacuum oven, Melrose Park, IL, USA) at 70 °C for 24 h. Approximately 80 % by mass of the initial ACP was retrieved after the ball milling and recovery process.

### Characterization of the Fillers

The amorphous state of both milled and unmilled ACP powders was verified by powder X-ray diffraction (XRD: Rigaku X-ray diffractometer, Rigaku/USA Inc., Danvers, MA, USA) and Fourier-transform spectroscopy (FTIR: Nicolet Magna-IR FTIR System 550 spectrophotometer, Nicolet Instrument Corporation, Madison, WI, USA). The wavelength accuracy of FTIR measurements was  $\leq 0.01 \text{ cm}^{-1}$  at  $2000 \text{ cm}^{-1}$ . Particle size distribution (PSD) of the fillers was determined by a laser light scattering technique (PSD: Microtrac 3501 particle size analyzer, East Coast Instrumentation, Egg Harbor Township, NJ, USA), following

dispersion of the solids in isopropanol (presonicated samples; 3 repetitive runs per powder) and/or in the air (dry samples; 3 runs per powder). Morphological/topological features of the fillers were examined by scanning electron microscopy (SEM; JEOL 35C instrument, JEOL Inc., Peabody, MA, USA) after the specimens were sputter-coated with gold.

### Resin Formulation

The experimental resin was formulated from the following commercially available dental monomers (ESSTECH): ethoxylated bisphenol A dimethacrylate (EBPADMA; mass fraction of 62.8 %), triethylene glycol dimethacrylate (TEGDMA; mass fraction of 23.2%), 2-hydroxyethyl methacrylate (HEMA; mass fraction of 10.4 %) and methacryloxyethyl phthalate (MEP; mass fraction of 2.6 %). The resin was photo-activated by the inclusion of camphorquinone (CQ; mass fraction of 0.2 %) and ethyl-4-N,N-dimethylaminobenzoate (4EDMAB; mass fraction of 0.8 %) as photo-oxidant and photo-reductant, respectively. The indicated acronyms will be used throughout this manuscript.

### ACP Composite and Copolymer (Unfilled Resin) Specimen Fabrication

Composite pastes were made from mixing the EBPADMA/TEGDMA/HEMA/MEP (ETHM) resin (mass fraction 60 %) and either unmilled or milled Zr-ACP filler (mass fraction 40 %) by hand spatulation. The homogenized pastes were kept under a moderate vacuum (2.7 kPa) overnight to eliminate the air entrained during mixing. The pastes were placed into Teflon molds 15.8 mm to 16.8 mm in diameter and 1.5 mm to 2.1 mm in thickness for biaxial flexure strength (BFS) testing; 5.8 mm to 6.1 mm in diameter and 3.0 mm to 3.1 mm in thickness for diametral tensile strength (DTS) testing; and 29.2 mm to 30.3 mm in length, 3.7 mm to 4.1 mm in width, and 3.1 mm to 3.3 mm in thickness for flexural strength (FS) testing. Each opening of the mold was covered with a thin Mylar film and a glass slide, which were clamped in place by spring clips. The clamped specimens were photo-polymerized by irradiating sequentially each face of the mold assembly for 120 s with visible light (Triad 2000, Dentsply International, York, PA, USA). The specimens were randomly selected and stored for 24 h at 22 °C in air before being tested for dry strength. The remaining specimens were immersed in distilled water at 22 °C for one month prior to testing for wet strength. The identical procedure was utilized in the fabrication and testing of unfilled copolymer specimens.

### Mechanical Testing

BFS, DTS, and FS were determined using a computer-controlled Universal Testing Machine (Instron 5500R, Instron Corp., Canton, MA, USA) operated by Instron Merlin Software Series 9.

For BFS measurements (number of specimens per group,  $n \geq 7$ ), the strength of a disk specimen supported along a lower support circle was determined under a static load utilizing a piston-on-three-ball loading arrangement with a crosshead speed of 0.5 mm/min. The failure stress was calculated according to the following equation [6]:

$$BFS = AL/t^2 \quad (1)$$

where  $A = -[3/4v(X-Y)]$ ,  $X = (1+v)\ln(r_1/r_s)^2 + [(1-v)/2](r_1/r_s)^2$ ,  $Y = (1+v)[1+\ln(r_{sc}/r_s)^2]$ , and where  $v$  = Poisson's ratio,  $r_1$  = radius of the piston applying the load at the surface of contact,  $r_{sc}$  = radius of the support circle,  $r_s$  = radius of disk specimen,  $L$  = applied load at failure, and  $t$  = thickness of disk specimen.

DTS specimens ( $n \geq 5$ ) were compressed to fracture using a flat circular head with a crosshead speed of 10 mm/min. The moist filter paper was placed above and below the specimen to prevent slipping during compression. DTS values were calculated according to the following equation [7]:

$$DTS=2L/\pi Dt \quad (2)$$

where:  $L$  = applied load at failure,  $D$  = diameter of disk specimen, and  $t$  = thickness of disk specimen.

FS tests ( $n \geq 7$ ) were performed as standard three-point flexure tests with lower reactionary supports spaced 20 mm apart at a crosshead speed of 0.5 mm/min. FS values were calculated as [7]

$$FS=3Ld/2wt \quad (3)$$

where  $L$  = maximum load at the point of fracture,  $d$  = distance between the supports,  $w$  = width of the specimen and  $t$  = thickness of the specimen. Young's Modulus ( $E$ ;  $n \geq 7$ ) was calculated from the FS data plots as the ratio of the elastic stress to the elastic strain (a slope of the linear region) [7].

### Water Sorption

To determine water sorption (WS) of copolymers and composites, a minimum of 15 pieces of specimens fractured during mechanical testing were dried over anhydrous  $\text{CaSO}_4$  until a constant mass was achieved ( $\pm 0.1$  mg). The specimens were then exposed to an air atmosphere of 75 % relative humidity (rH) at room temperature (22 °C) by keeping them suspended over saturated aqueous NaCl slurry in closed systems. Gravimetric changes were recorded at one week intervals of exposure to this rH up to 7 weeks. The WS (a percent mass fraction) of any individual specimen at any given time interval ( $t$ ) was calculated according to the expression:

$$WS = \left( \frac{W_t - W_o}{W_o} \right) * 100 \quad (4)$$

where  $W_t$  represents specimen mass at the time  $t$ , and  $W_o$  is the initial mass of the dry specimen.

### STATISTICAL ANALYSIS

One standard deviation (SD) is given in this paper for comparative purposes as the estimated standard uncertainty of the measurements. These values should not be compared with data obtained in other laboratories under different conditions. Experimental data were analyzed by ANOVA ( $\alpha = 0.05$ ). Significant differences between specific groups were determined by pairwise multiple comparisons (two-tail t-test; unequal variances).

### RESULTS

FTIR spectra and XRD patterns of the unmilled and milled Zr-ACP utilized in this study (Figures 1 and 2, respectively) revealed no differences in their structural features. FTIR spectra of the unmilled and milled powder exhibited two wide absorbance bands (Figure 1), i.e.,  $\nu_1$  and  $\nu_3$ ,  $\text{PO}_4$  stretching ( $1200$  to  $900$ )  $\text{cm}^{-1}$  and  $\nu_1$   $\text{PO}_4$  bending ( $630$  to  $500$ )  $\text{cm}^{-1}$ . Corresponding XRD readings (Figure 2) consisted of two diffuse, broad bands characteristic of such commonly recognized noncrystalline substances as glasses and certain polymers. The FTIR and XRD screening of the milled ACP confirmed that milling with isopropanol and the subsequent drying procedure did not compromise the amorphous character of the filler.

Dry PSD analysis (Figures 3a and 3b; performed without presonication and by dispersing ACP in the air) showed a reduction in median diameter ( $d_m$ ) from ( $40.45 \pm 44.41$ )  $\mu\text{m}$  to ( $22.91 \pm 20.80$ )  $\mu\text{m}$  for unmilled vs. milled ACP. When ACP was sonicated before the measurement (and dispersed in isopropanol)  $d_m$  was reduced from ( $27.48 \pm 19.03$ )  $\mu\text{m}$  to ( $9.98 \pm 8.07$ )  $\mu\text{m}$  (Figures 3c and 3d).

The results of the BFS testing of dry and wet composite and copolymer specimens are illustrated in Figure 4. The average BFS values for both dry and wet specimens decreased in the following order: copolymer > milled ACP composites > unmilled ACP composites. Exposed to the aqueous environment, unmilled ACP composites lost approximately ¼ of their dry state strength. However, the biaxial flexural strength of milled ACP composite, similar to the copolymer specimens, did not deteriorate upon soaking.

The average dry and wet FS values of copolymer and composites (Figure 5) showed the same trend as that seen with the average BFS values of these specimens: copolymer > milled ACP composites > unmilled ACP composites. The 34 % decrease in FS upon immersion (wet vs. dry specimens) seen in unmilled ACP composites was significant. However, the apparent decreases in the FS of wet vs. dry copolymer and milled ACP composite specimens (10 % and 14 %, respectively) were not significant. Contrary to the BFS and FS test results, the average DTS values of both dry and wet unmilled and milled ACP composites were significantly lower than the DTS of copolymer specimens (Figure 6). The unmilled composite specimens showed further deterioration in strength upon aqueous immersion. The apparent decrease in the DTS of wet vs. dry copolymer specimens was not statistically significant.

The average values of the elastic modulus (Figure 7; presented as the mean values of combined dry and wet specimens since the pre- to post-soaking tests showed no significant differences) for the unmilled and milled ACP composites ( $3.7 \pm 0.9$ ) GPa were, expectedly, higher than the average value of copolymers ( $2.6 \pm 0.5$ ) GPa. These values of E are nearly 50% lower than that of another commercially available ion-releasing composite ( $(7.3 \pm 0.8)$  GPa) [8].

Comparisons of the maximum levels of WS (mass fraction, %) following the 39 d of exposure to 75 % rH for copolymers, unmilled ACP composites and milled ACP composites are given in Figure 8. Copolymers and the milled ACP composites absorbed a maximum mass fraction of ( $1.43 \pm 0.35$ ) % and ( $1.55 \pm 0.49$ ) % water, respectively. However, composites based on the unmilled ACP absorbed almost 50 % more water [maximum mass fraction of ( $2.28 \pm 0.60$ ) %] than the milled ACP composites. The lower water uptake of the milled ACP composites may also influence interfacial bonding of the matrix/filler phases, and in turn their mechanical strength, as has previously been demonstrated [9–10].

## DISCUSSION

The median particle size ( $d_m$ ) is used here to show the effects of milling, but it should be noted that this measure provides very little information about the particle size distribution of the sample. A complete characterization required both quantitative (PSD) and qualitative (SEM) analysis.

Given the tendency of dry ACP to agglomerate, it was necessary to perform particle size analysis on both dry and presonicated samples. Tests were performed several times from different parts of each sample to establish repeatability. Since dry filler is used in the fabrication of specimens, the analysis of dry ACP with no sonication better reflects the particle size distribution within the composites. On the other hand, sonicating and dispersing ACP in isopropanol before measurement is more representative of the true particle size distribution because it breaks up the large agglomerates that form spontaneously in the dry sample.

In both cases, the milled ACP showed a sharper distinction between small and large particles. The multimodal distributions obtained from particle size analysis of the milled powder are consistent with this observation. Corresponding SEM microphotographs of the unmilled and milled ACP powder (Figures 9a and 9b) show that similar agglomeration occurs in both samples, which tends to overshadow any textural or morphological differences that may exist between the two. It is clear, however, that the milled sample contains a significantly higher

volume of fine particles. A comparison of dry PSD analysis confirms this observation; 18.06 % of milled particles are under 1  $\mu\text{m}$  in diameter, compared to only 1.43 % for unmilled ACP.

Confirmation of this observation was also obtained during the fabrication of ACP composite specimens. Hand spatulation of milled ACP filler (mass fraction 40 %) into the ETHM resin proved very easy and took only five minutes, while the same process using unmilled ACP (mass fraction 40 %) can take up to three times as long. In addition, the homogenized pastes have significantly different handling characteristics. Paste with milled ACP is runny and very flowable, while paste with unmilled ACP is extremely viscous and not at all flowable. Increasing the mass fraction of milled ACP in 2 % increments showed that approximately 80 mass % of milled ACP is needed to obtain handling properties similar to a composite paste with 40 mass % unmilled ACP. This, along with the obvious differences in handling properties, provides clear evidence of a reduction in the average size of particles and agglomerates.

As expected, two-tail t-tests showed milled ACP composites performed significantly better in both flexure and biaxial flexure than unmilled ACP composites. The narrower particle size distribution obtained through milling improved dispersion of the filler within the matrix, minimizing the gaps between particles and allowing them to fit into the resin matrix more efficiently [11]. The overall number of voids appeared to decrease and the mechanical properties of the composite were in turn improved. Evidence of this correlation has been established through FTIR microscopy [4].

Ideally, a material subjected to a diametral compression test will expand across the diametral plane in a manner equivalent to that which would be produced by a tensile stress applied in the same direction. Copolymer specimens, however, are much less brittle than either unmilled or milled ACP composites. Thus, when subjected to a compressive load, the material deforms plastically and small flat areas develop at the specimen contact points. Prisms begin to develop at these points, redistributing stresses and often causing failure in shear. This leads to a significant deviation from the idealized pure tension across the diameter and likely accounts for the gap between the DTS of copolymer specimens and the DTS of milled and unmilled specimens.

It has been acknowledged that porosity and poor interfacial bonding between a filler particle and a resin matrix can act as flaws within a microstructure which, when subjected to sufficient stresses and/or aqueous challenge, can lead to premature specimen failure [11]. Care must therefore be taken in the fabrication of composites for experimental and clinical applications to ensure that a minimum of defects are introduced into the structure. Poor processing techniques such as inefficient packing of composite pastes into molds can lead to internal inclusions (i.e., air bubbles) within the structure, which can in turn lead to failure [12]. Surface finishing can be used to reduce edge effects in flexural and biaxial flexural specimens (Waterproof Silicon Carbide Paper, FEPA P #1200), as well as to eliminate surface pores and scratches that might otherwise act as stress concentrations.

## CONCLUSIONS

As a result of the mechanical milling, the average particle size (expressed as the median diameter) of ACP filler was reduced by 64 % in its wet state (dispersed in isopropanol), and 43 % in its dry state. Marked improvements in biaxial flexure strength and moderate improvements in flexural strength upon aqueous exposure of milled ACP composites are attributed to the more homogeneous distribution of the finer ACP particles within the composite. The reduced water sorption of the milled ACP composites is linked to a lesser number of voids/defects existing throughout the body of composite disk specimens. However, the diametral tensile strength and Young's Modulus of composites appeared to be less affected

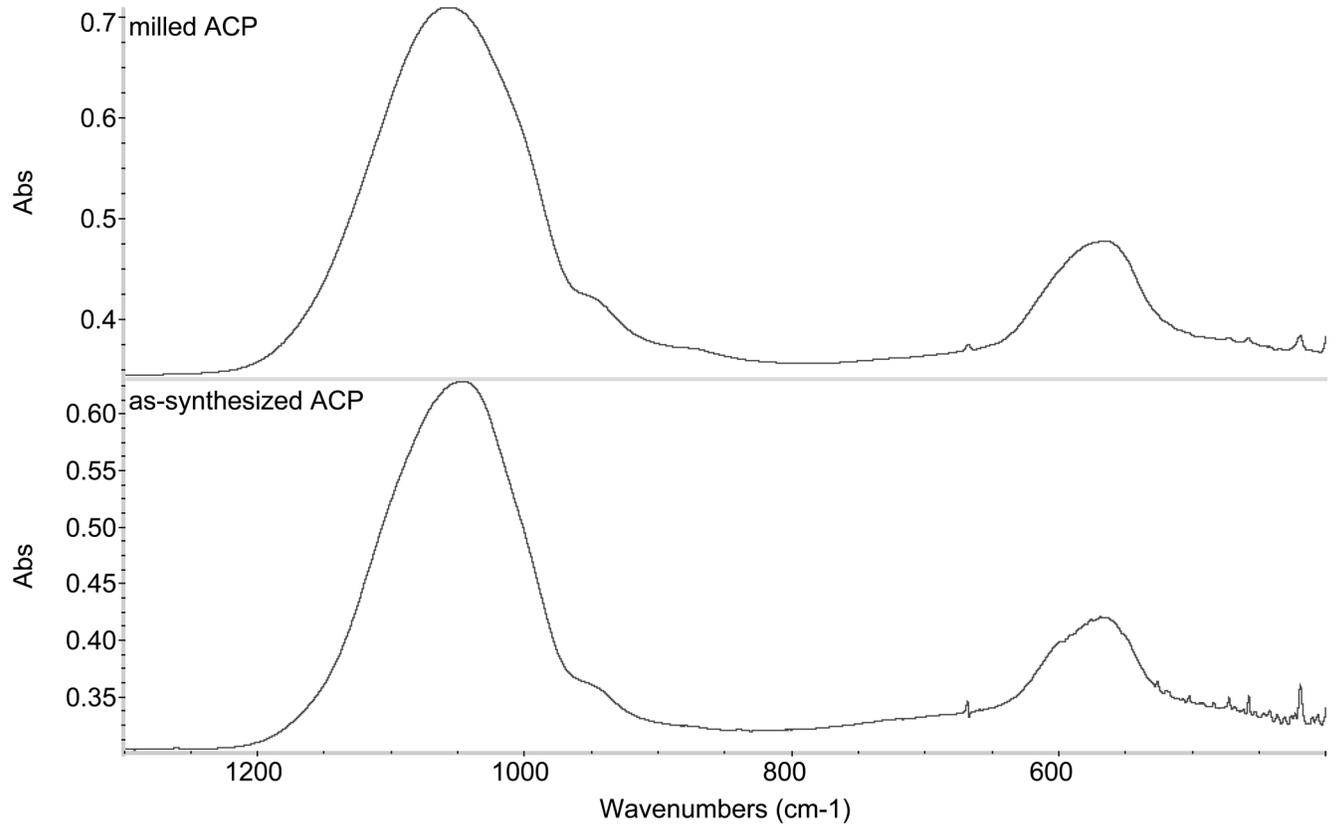
by milling of the filler in both dry and wet stage. Mechanical milling is established as a promising tool for reducing the size and number of large, coarse particles that exist in as-synthesized ACP. Modifications in the milling protocol are needed to further improve the mechanical interlocking at the filler/matrix interface, which might, in turn, boost the mechanical performance of composites.

### Acknowledgements

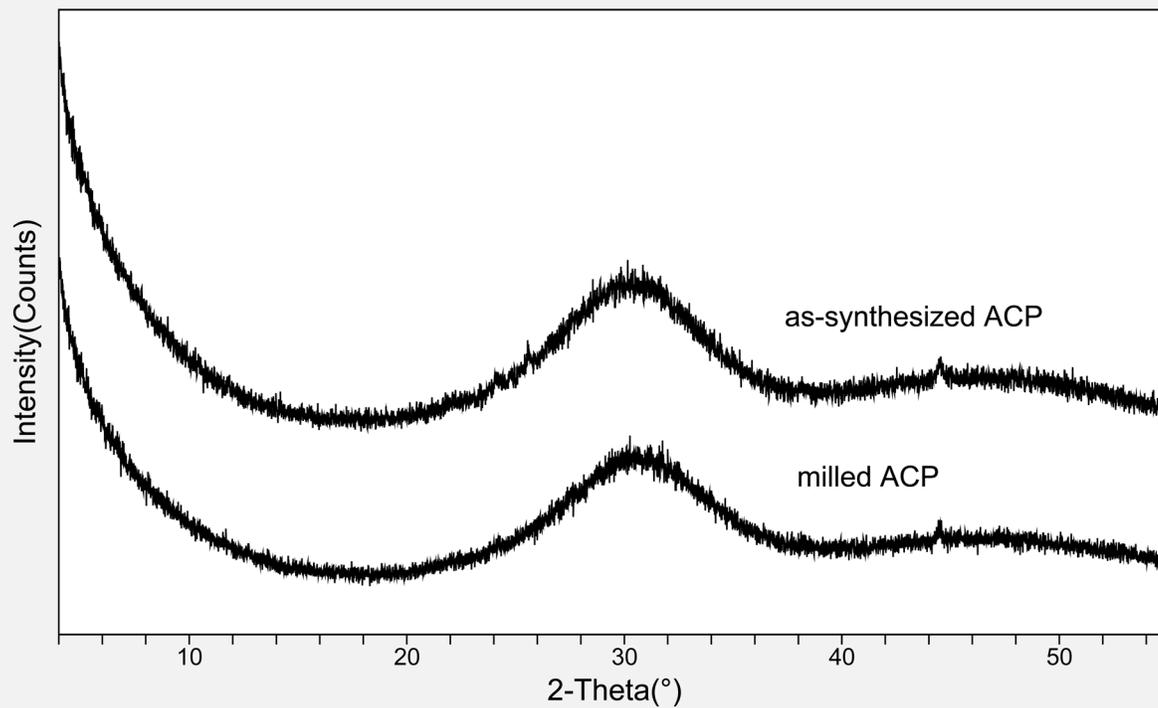
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**Figure 1.** Typical FTIR spectrum of the unmilled and milled ACP utilized in the study.

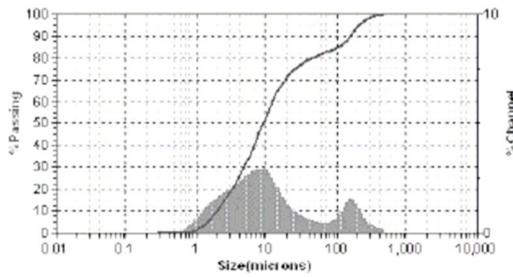


**Figure 2.**  
X-ray diffraction patterns of the unmilled and milled ACP filler presented in Figure 1.

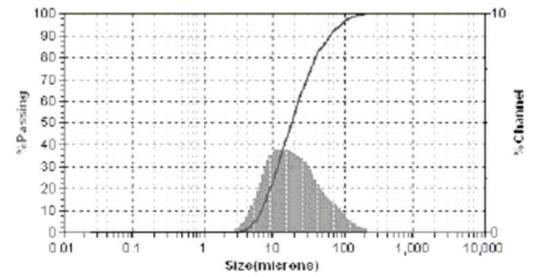
3a

unmilled ACP

3c



dry

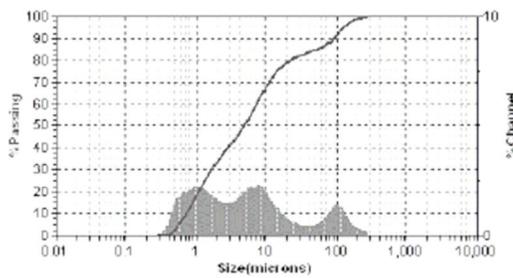


presonicated in isopropanol

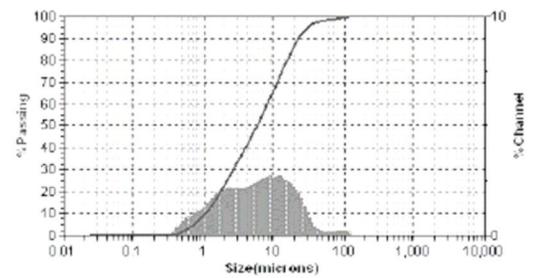
3b

milled ACP

3d



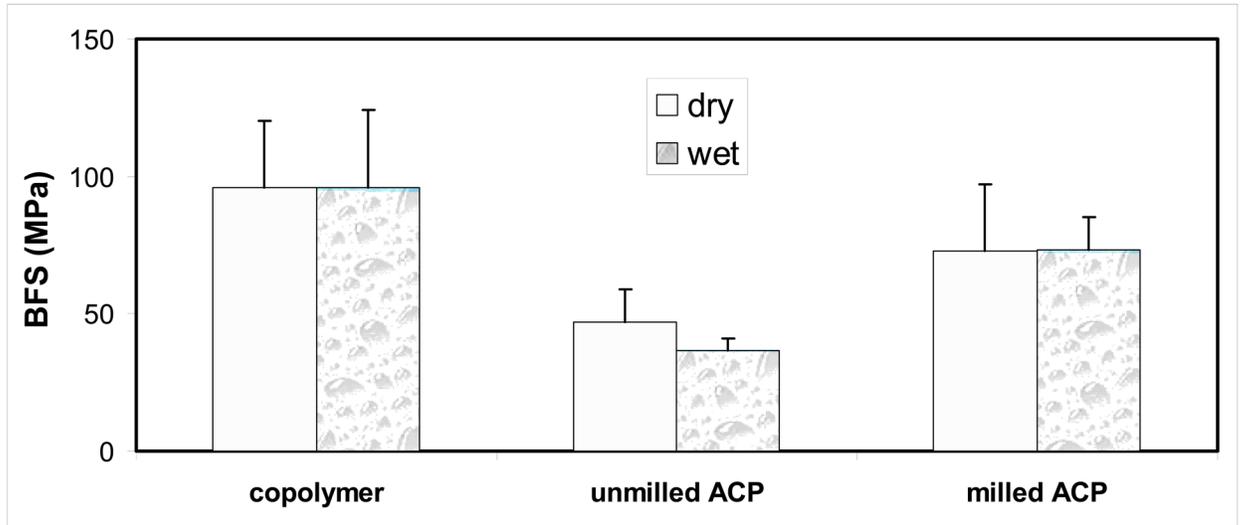
dry



presonicated in isopropanol

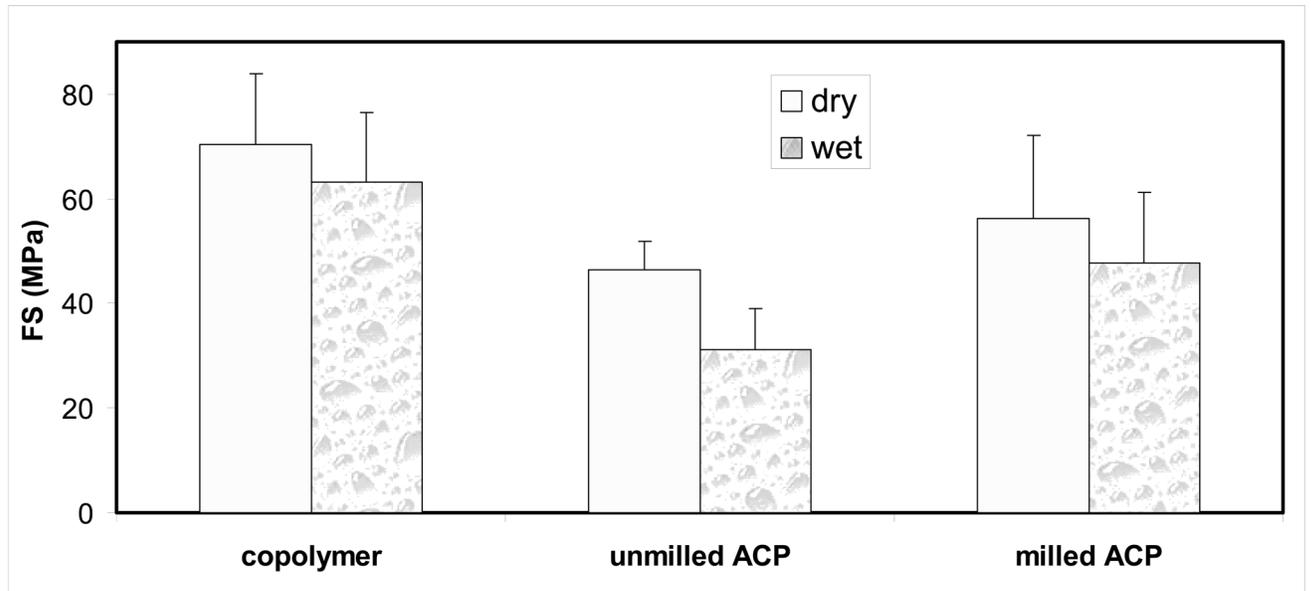
**Figure 3.**

Particle size distribution of the unmilled ACP and milled ACP filler, both dry and following sonication in isopropanol.

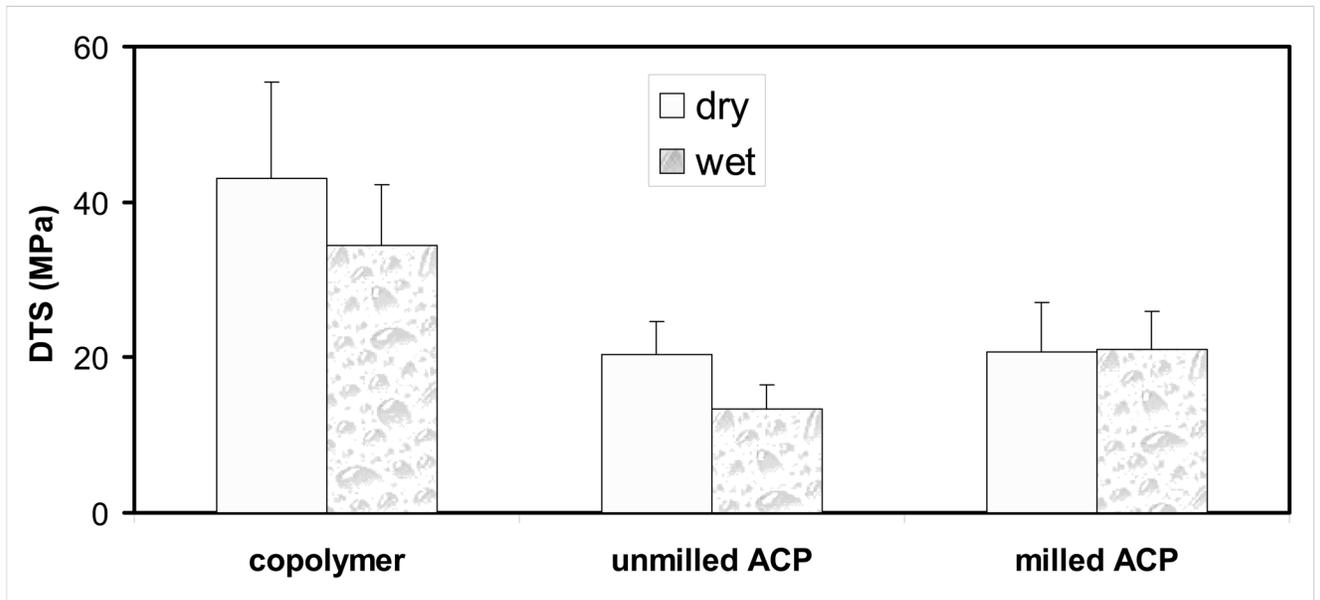


**Figure 4.**

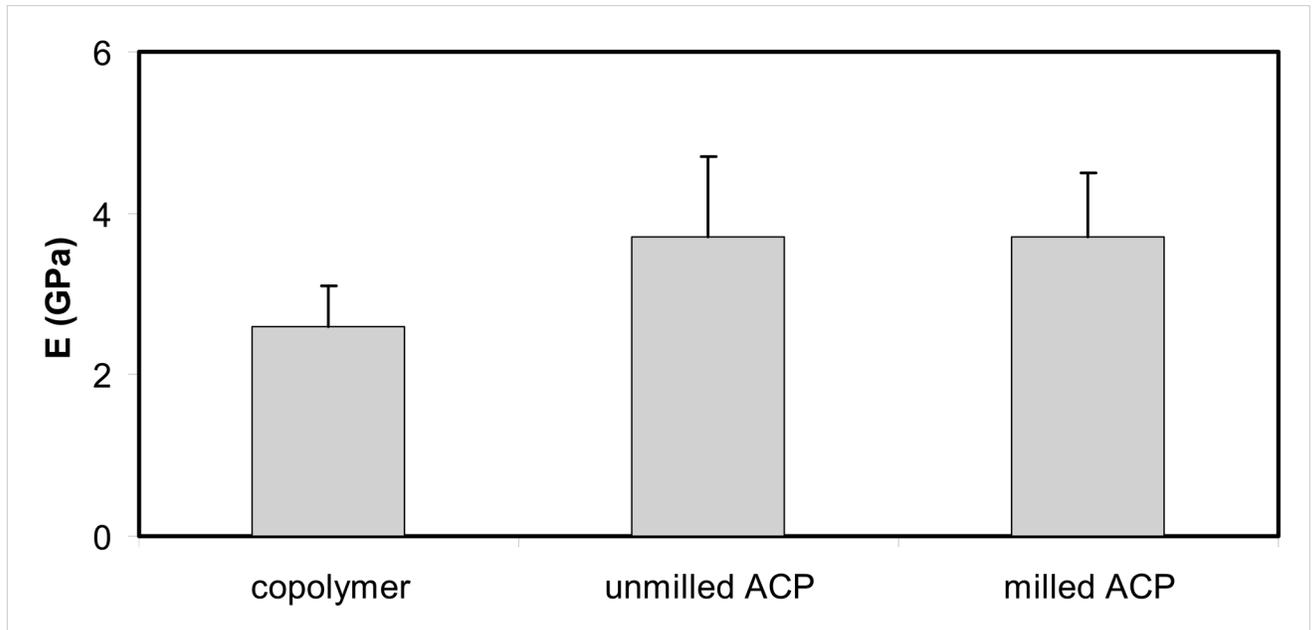
Mean values of the BFS recorded for dry and wet copolymer, unmilled ACP composite and milled ACP composite specimens. Number of specimens in each experimental group was  $n \geq 7$ . The standard deviation (SD; indicated by a bar) is taken as a measure of the standard uncertainty in Figures 7–11.



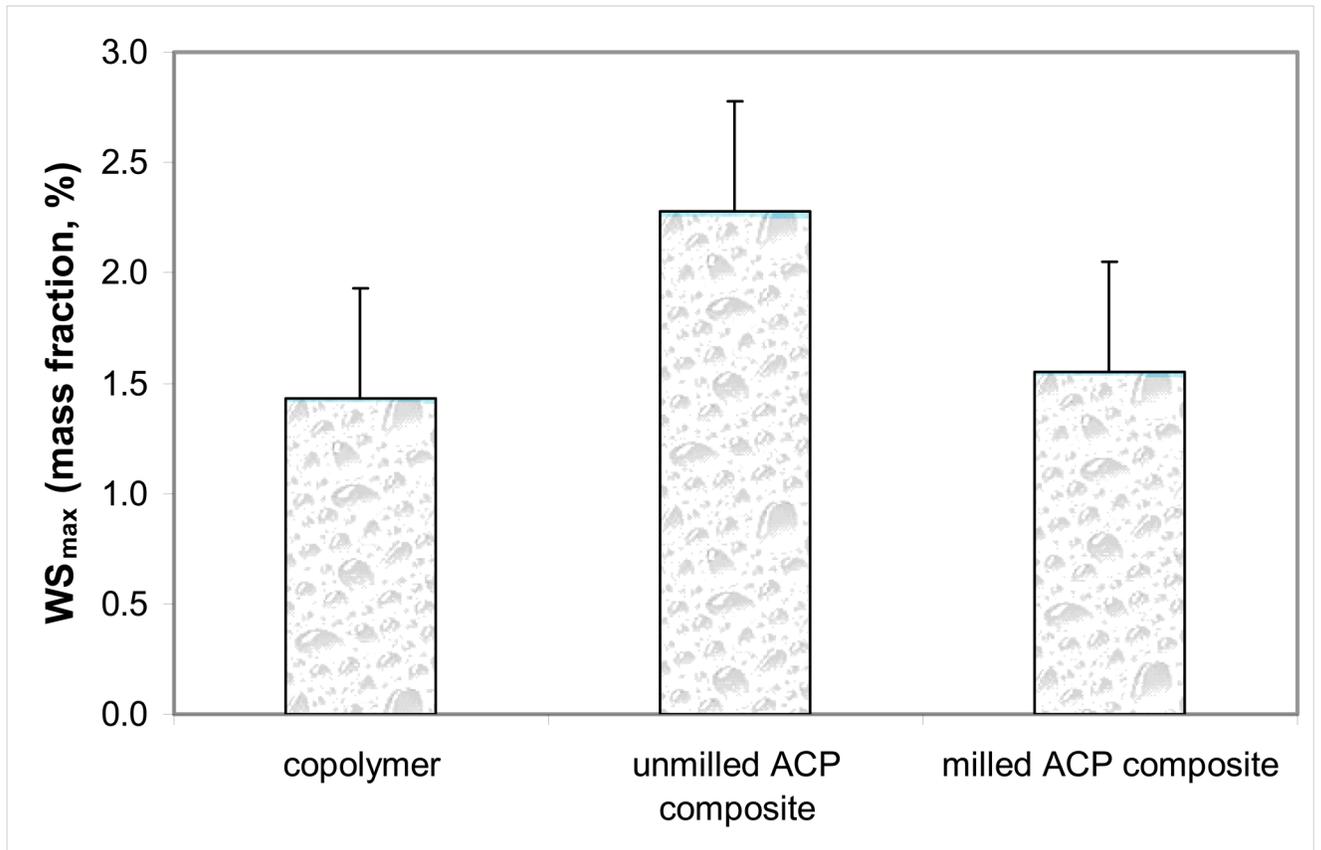
**Figure 5.** Mean values of the FS recorded for dry and wet copolymer, unmilled ACP composite and milled ACP composite specimens ( $n \geq 7$ ).



**Figure 6.** Mean values of the DTS recorded for dry and wet copolymer, unmilled ACP composite and milled ACP composite specimens ( $n \geq 5$ ).

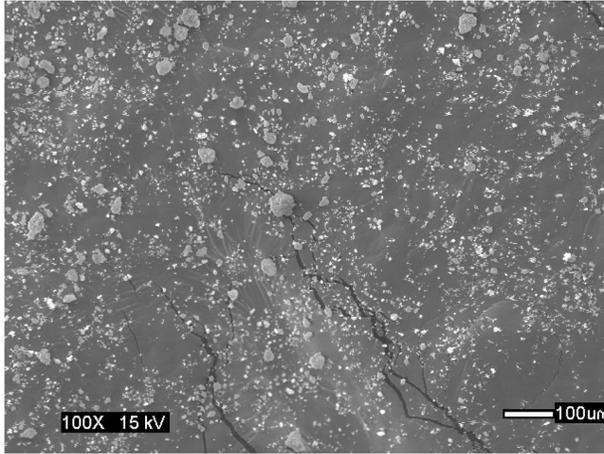


**Figure 7.** Mean values of the Young's Modulus (E) calculated for the copolymer, unmilled ACP composite and milled ACP composite specimens ( $n \geq 38$ ).



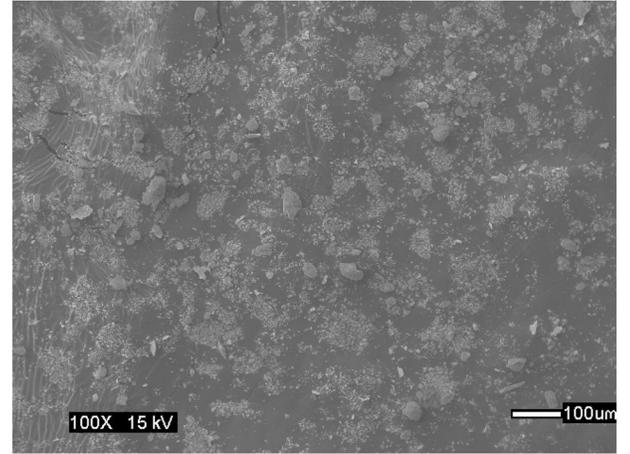
**Figure 8.** Maximum water sorption (WS) values (mean + SD) of dry and wet copolymer, unmilled ACP composite and milled ACP composite specimens ( $n \geq 7$ ).

unmilled ACP



9a

milled ACP



9b

**Figure 9.** Microphotographs showing a typical morphology of the unmilled ACP and milled ACP filler (scanning electron microscopy data).