The effect of acidic treatment of carbon fiber on denture mechanical properties

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Abstract. The purpose of this research is to increase the mechanical properties (impact and flexural strength) of acrylic polymethyl methacrylate (PMMA) denture base resin by incorporated treated and coated woven carbon fiber (WCF). To increase the roughness of fibers, WCF treated with para-aminobenzoic acid (PABA), (C₇H₇NO₂) at 3 different concentration treatments (0.10, 0.15, and 0.20 M). In order to make the samples appears with good aesthetic and bonding, WCF was coated with β-Tricalcium phosphate (β-TCP) powder with (0.08, 0.10, and 0.12) weight fraction (wi) in addition of using polyvinyl alcohol (PVA) at 0.01 wi, respectively. After 10 days of water storage at room temperature, the specimens have been tested via using the Charpy effect measuring system and three-point bending tests. The mechanism of interfacial interaction between β-TCP and woven carbon fibers was investigated by field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR). Based on the obtained results, when specimens contained treated and uncoated woven carbon fiber with a high concentration of (PABA), the impact and flexural strength were higher than pure sample but have a bad aesthetic. Further, (PMMA) reinforced with coated and treated woven carbon fiber as hybrid composites recorded very high raises in the mechanical properties when the concentration of (PABA) and (β-TCP) was increased, with a good aesthetic.

Keywords: Denture base, PMMA, PVA, Tri calcium phosphate, Woven CF, PABA.

1. Introduction.
Poly methyl methacrylate (PMMA) is the most successful candidate among many materials to fabricate denture base resin [1], due to its reasonable quality, low weight, excellent esthetic properties, and ease of processing and polishing and repair [2-4]. However, PMMA is not considered as a perfect material, because, its brittleness, inferior mechanical and physical properties, low modulus of elasticity, high coefficient of thermal expansion and low sorption, low flexural strength, and low impact strength [5,6]. These drawbacks of PMMA lead to the fracture, which is the most common problem of denture base resin [7]. There are many causes for fracture of the dentures, such as impact fracture usually occurs when a patient is coughing that pushes the dentures out of the mouth or accidentally dropping the dentures on the surface during the cleaning of dentures. Also, flexural failure of denture occurs when the concentration of stress around the micro cracks formed in the material due to the continuous applied of small forces [8]. Numerous methods have been developed to enhance the mechanical and surface properties of the acrylic resins. It was suggested that the introduction of synthetic fibers to the monomer/polymer is strengthening the result acrylic resin. Various fibers and powders such as carbon fiber [9,10], glass fiber [6, 11], aramid fiber [12], polyethylene fiber [13], zirconium oxide ZrO₂ nano-
particles [14] and kaolinite powder (Al$_2$Si$_2$O$_5$(OH)$_4$) [15] were used as reinforcements for denture base material. However, because of weak interface between fiber and resin affecting the mechanical properties, these fibers break-up the homogeneous matrix of acrylic resin. To avoid this problem, several studies have been reported in the literature that recommends surface treatment of fibers and incorporation ceramic powder such as (TiO$_2$, and TCP) [16] or metal oxides such as (MgO, and ZnO) [17].

In light of above notices, the research was considered to determine how mechanical properties (impact and flexural strength) of acrylic resin can be enhanced by the use of carbon fiber reinforcement and whether surface treatment affects the impregnation of fiber within the resin matrix. Hence, the purpose of the study is to determine some mechanical properties (impact and flexural strength) of PMMA resin, and studying the influence of woven carbon fiber (treated and coated) on impact and flexural strength with good aesthetic.

2. Experimental details

2.1 Acidic treatment:

Fig. 1 displays untreated carbon fiber in woven form. Woven carbon fibers (product No: CR160K, weight 600 g/m$^2$, thickness: 0.333 mm, Japan) were cut into (70×50 mm$^2$).

![Figure 1. Untreated carbon fiber in woven form.](image)

The woven carbon fiber was impregnated in ethanol for 15 minutes to remove contaminants, and then they were put on filtering paper, therefore put in an oven at 50 °C for 30 min, for drying. To make an acidic solution, (3 g) benzoic acid (3-Amino benzoic acid, C$_7$H$_7$NO$_2$, pure, minimum Assay: 98 %, New Delhi-110002, India) was dissolved in (100, 150, 200 ml) of distilled water, and left for 20 min on the magnetic stirrer. The woven carbon fiber immersed in an acidic solution for 3 hours. Once the immersion time ended, the fibers were rinsed thoroughly with distilled water to remove acidic influence. Finally, the woven fiber was dried in an oven at 70 °C for 2 hours.

2.2 Coating of carbon fibers

Dark carbon fiber coating with tri-calcium phosphate: different weight proportions of Tri-calcium phosphate average size (43.31nm), as presented in Table 1, were mixed with (10 ml) of distilled water and left with continuous stirring. PVA was added to the β-TCP solution with heating (Hot plate with a magnetic stirrer, BOECO-Germany), until the solution became cloudy. The coating solution was added
to fibers and left overnight in order to dry. This coating technique gave the fibers a white color on their surface. Fig. 2 referred to carbon fiber after coating.

![Figure 2. Woven carbon fiber after coating.](image)

**Table 1.** Composition of the specimens prepared.

| Group no. | WCF (wi) | TCP (wi) | PVA (wi) | PMMA (wi) | Treatment concentration (M) |
|-----------|----------|----------|----------|-----------|----------------------------|
| G1        | -        | -        | -        | 1         | -                          |
| G2        | 0.04     | -        | -        | 0.96      | 0.10                       |
| G3        | 0.04     | -        | -        | 0.96      | 0.15                       |
| G4        | 0.04     | -        | -        | 0.96      | 0.20                       |
| G5        | 0.04     | 0.08     | 0.01     | 0.87      | 0.10                       |
| G6        | 0.04     | 0.10     | 0.01     | 0.85      | 0.10                       |
| G7        | 0.04     | 0.12     | 0.01     | 0.83      | 0.10                       |
| G8        | 0.04     | 0.08     | 0.01     | 0.87      | 0.15                       |
| G9        | 0.04     | 0.10     | 0.01     | 0.85      | 0.15                       |
| G10       | 0.04     | 0.12     | 0.01     | 0.83      | 0.15                       |
| G11       | 0.04     | 0.08     | 0.01     | 0.87      | 0.20                       |
| G12       | 0.04     | 0.10     | 0.01     | 0.85      | 0.20                       |
| G13       | 0.04     | 0.12     | 0.01     | 0.83      | 0.20                       |

### 2.3 Preparation of the flask

Denture base samples were fabricated by using a special flask as illustrated in Fig.3. The flask consists of two parts: upper and lower. The kaolin piece (70×50×3 mm) was placed in the lower part. Next, the dental stone powder was mixed with water and poured the stone to fill the flask. The inner surface of each part of the flasks was coated with Vaseline to keep the dental stone from binding to the flask. The flask was hitting several times to remove bubbles, which may be found inside the stone. The final set of the dental stone, the flask left for 15 min for hardening, and then the flask opened carefully and removes excess kaolin and stone. The obtained flask was shown in Fig. 3.
2.4 Preparation of the samples

Thirteen groups of test specimen were prepared by the heat-cured of PMMA, consisting of powder and liquid (methyl methacrylate, MMA) (2 g/1 ml) according to the manufacturer's instructions. In a clean and dry mixing jar the powder was mixed with liquid (MMA) and allows each powder to be wetted by monomer and left until it reaches a consistency appropriate for packing, during this time, the cover should be positioned over the mixing jar to prevent monomer evaporation and left to stand at room temperature for (12-16) min until reached to the dough stage, as shown in Fig. 4. For the unreinforced dough (G1) was placed in the mold directly. For the reinforced samples (G2-C13), the MMA has been used to wet woven carbon fibers with and without coating for 2 min. The dough was cut into two sheets; woven carbon fiber was placed between halves of the dough. Hydraulic pressure was applied to the flask slowly to 1Ton for 5 min. before the polymerization reaction. Then immerse the flask in cold water and waiting until water boiling. The resin was cured in boiling water for 1 h according to the manufacturer’s instructions. When polymerization was completed; the molds extracted from water and left to cool at room temperature. The test samples were smoothed with 400,600 and 800 silicon carbide paper under tap water to remove excess materials, and then cut into specific dimensions to all tests. Before testing, all test samples were stored in water at 37°C for 10 days. All specimens were shown in Fig. 5.

Figure 3. Flask of samples.

Figure 4. The dough stage.
2.5 Structural properties:

2.5.1 Fourier Transform Infrared Spectroscopy (FTIR):

The FTIR spectra of untreated and treated carbon fibers with para-aminobenzoic acid were recorded in the range of 400-4000 cm$^{-1}$ by using an FTIR machine (SHIMADZO IRFFINITY) to identify the functional groups in untreated and treated fibers.

2.5.2 Field Emission Scanning Electron Microscopy (FESEM):

The surface microstructure of untreated and treated, with and without coating woven carbon fiber was examined utilizing Field Emission Scanning Electron Microscopy type (MIRA3 TESCAN-XMU).

2.5.3 Mechanical properties:

Impact strength and flexural strength were performed with utilizing the same methods in reference [15].

3. Results and discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR was used to analyze surface functional groups of woven carbon fibers. The FTIR spectra can provide precise information on the material surface functional groups of untreated and treated WCF via benzoic acid. Fig. 6 shows the FTIR spectra of untreated and treated WCF using (0.10, 0.15, and 0.20 M) PABA. The spectrum of untreated carbon fiber shows a peak at 3429 cm$^{-1}$ attributed to O-H stretching vibration of the absorbed water on the fiber surface and followed by another adsorption around 2962 cm$^{-1}$ attributed to the stretching vibration from saturated hydrocarbon C-H [18]. The band near 2366 cm$^{-1}$ dedicated to C≡C stretching peak, the characteristic peaks at 1722 cm$^{-1}$, 1637cm$^{-1}$, and 1230 cm$^{-1}$ represent to C=O stretching peaks, C=C stretching, and C–N stretch peak respectively [19]. When compared untreated with treated WCF, some new peaks can be observed for treated carbon fiber. In any concentrations of PABA, WCF was recorded amine functional group in the FTIR spectrum. Peaks at 3423 cm$^{-1}$ (0.20 M), 3451 cm$^{-1}$ (0.15 M), and 3624 cm$^{-1}$ (0.10 M) denote the N-H functional group,
stretched as a result of the vibration of the amine group. The characteristic of the oxygen function existed in C=O stretching, which appears at 1647 cm\(^{-1}\) for three concentrations, while C‒O stretching appears at 1249 cm\(^{-1}\) peak when WCF treated with (0.20 M) and (0.15 M) while disappearing at (0.10 M) concentration. The oxygen content increased via increasing the concentration of PABA [20]. The most intensity is related to the C‒N recorded at 1174 cm\(^{-1}\) when WCF treated with (0.15 M) [21]. In the preparation of biocomposites, WCF treated by PABA is essential; liquid chemical oxidation through PABA makes it an efficient technique to change the inert surface of WCF.

![Figure 6. FTIR of WCF before and after treatment with PABA.](image)

### 3.2 Field Emission Scanning Electron Microscope (FESEM)

Fig. 7a shows the surfaces of untreated woven carbon fibers appear smooth without any impurity. FESEM examination for the treated and coated surface of woven carbon fiber was imaged. The FESEM photographs of treated and coated fiber show regular and perfect spherical crystal nanostructures particles have been grown as individual clusters with few agglomerates over the surface of WCF. It can be shown that the β-TCP coating has grown homogeneously and the adhesion between the fiber and the β-TCP coat has improved. The cause for such adherence is due to the functional group of para aminobenzoic acid that has been created in carbon fiber. Fig. 7c and d showed the higher density of the functional groups of PABA results in an increase in the roughness of the surface of WCF, thus the interfacial chemical bonding strength between coatings /fiber and the resin was improved. It is assumed that the increased roughness of the fiber can enhance a mechanical interlocking effect between the fiber and the coating; this description is in accordance with Tao et al [22]. Fig. 7e shows the average particle diameter of β-TCP was 43.31nm with a spherical shape.
Figure 7. FESEM of (a): untreated and uncoated of CF (b) CF treated at 0.10 M of PABA and coated with β-TCP (c) CF treated at 0.15 M and coated (d) CF treated at 0.20 M and coated (e) β-TCP particle.

3.3 Impact strength

Table 2 illustrates the impact strength findings for the control group, and samples developed with treated WCF with PABA. All samples have the same fiber content (0.04 wi) and are treated with different concentrations of Para-aminobenzoic acid (0.10, 0.15, 0.20 M).

| Group no. | Impact strength (KJ/m²) |
|-----------|------------------------|
| G1        | 8.05                   |
| G2        | 5.3                    |
| G3        | 9.51                   |
| G4        | 9.87                   |

The control group recorded impact strength of 8.05 KJ/m². Lowest value of impact strength is observed in G2 when compared with the control group. The impact strength decreased with lower PABA concentration at 0.10 M, it is known that the mechanical properties depend on the bonding and interface between fiber and polymer. In G2 the surface of carbon fiber is smooth as shown in FESEM micrograph 7 b, leading to poor initial bonding between fiber and matrix. For this reason, G2 gave poor interfacial regions, hence recorded low impact strength. The highest impact strength was recorded when the fiber was treated via (0.15 M, 0.20 M). From this result, the impact strength increased with higher PABA concentration. This is because the roughness of carbon fiber surface occurs in higher acidic concentration, resulting in good bonding between carbon fiber and matrix. Despite the rise in the impact strength of the composites, the aesthetic-related result is negative.

Table 3 display the impact strength values of coated and treated WCF with β-TCP and PABA acid respectively.

| Group no. | Impact strength(KJ/m²) |
|-----------|------------------------|
| G1        | 8.05                   |
| G5        | 6.9                    |
| G6        | 7.3                    |
| G7        | 7.8                    |
| G8        | 10                     |

Table 3. The impact strength values of coated and treated WCF.
For (G5, G6, and G7) samples prepared by treated WCF with PABA concentration (0.10 M) and coated with $\beta$-TCP (0.08, 0.10, and 0.12 wi) respectively, the impact strength values decreased when compared with G1. This decrement is because a bad bonding among coating, fiber, and the matrix, due to the poor acidic treatment of WCF. After treatment CF with the dilute solution still smooth as shown in FESEM micrograph (7 b), the bonding strength between carbon fiber, $\beta$-TCP powder and a matrix is poor. Groups G8, G9, and G10 are related to samples reinforced by treated WCF with (0.15 M) of PABA concentration and coated with (0.08, 0.10, and 0.12 wi) of $\beta$-TCP. The addition of any content of $\beta$-TCP powder at any weight fraction leads to increases in the value of impact strength when comparison with G1. One can explain that the $\beta$-TCP coatings presence, varying the CF surface characteristics into hydrophilic, highly enhances the interfacial bonding strength via the direct adhesion to matrix [23]. The treatment of carbon fiber by PABA concentration (0.15 M) had a positive effect on impact strength. This is because of the interfacial shear strength between matrix and fiber is high. The impact strength of hybrid samples papercd by treated woven fiber with a concentrated solution of PAPA and coated with different weight fractions are illustrated in Table 3. The concentrated solution with the increment in the amount of $\beta$-TCP has a positive influence upon the impact strength values as depicted in (G11), (G12), and the value of impact strength raised from (15.6 KJ/m$^2$) to (17.45 KJ/m$^2$). For (G13) having a high content amount of $\beta$-TCP (0.12 wi), the impact strength increased to 20.23 KJ/m$^2$ by (151%) as compared with control group G1. That's perhaps owing to the reason that the $\beta$-TCP powder possesses a much higher strength of fracture in comparison with the PMMA resin [24]. Besides, the increment in the content of $\beta$-TCP raises strength. This is an anticipated result of the better adhesion of matrix and powder, and thus a higher permissible stress level transfers to CF through the loading. Mixing PVA with $\beta$-TCP powder enhance the mechanical properties of coatings because of its compatible structure and hydrophilic properties [25].

### 3.4 Flexural Strength

The flexural strength of acrylic resins is known to be the predominant form of clinical failure. The results of the flexural strength values in current study appeared as shown in Table 4, which shows a comparison between a pure sample and samples reinforced with carbon fibers treated with an acid solution at varying concentrations. The flexural strength of control group is 70.55 MPa, while samples prepared carbon fiber treated with a concentrated acid solution tends to be more efficient and has the maximum flexural strength value in G4. The explanation for this improvement is the etching process that produced apparent roughness of the surface fiber. The presence of roughness helped increase the area of the interlocking surface between the fiber and the matrix, which encourages the movement of stress from the matrix to the carbon fiber and therefore increased of the flexural strength. The researchers agree with this conclusion are Panigrahi, and Powel [26], Bismarck and Mohanty [27]. Eventually, a carbon fiber crack brings the test specimen to a complete fracture. This fact suggests that the tensile strength of the carbon fiber is part of the test specimen's flexural strength [28].

| Group no. | Flexural strength (MPa) |
|-----------|-------------------------|
| G1        | 70.55                   |
| G2        | 76.93                   |
| G3        | 81.9                    |

Table 4. Descriptive data of flexural strength.
Flexural strength values for reinforced PMMA with treated and coated carbon fiber hybrid samples were summarized in Table 5. In current study, the flexural strength in G7 was significantly better than control group G1, while other samples recorded findings for the flexural strength less than the pure sample. The reason may be due to the weak bond between the coating and the resin, which gives low values of flexural strength. The bending strength was higher after the introduction of treated carbon fibers with concentrations of PABA at (0.15 M) and (0.20 M) and also coated with different ratios of β-TCP when compared with the pure sample. The increment in the flexural strength findings by using woven carbon fiber treated with and with 0.15 M of PABA (G8, G9, and G10) are (19.44, 17.5, and 15.09) % and fibers treated by 0.20 M of PABA (G11, G12, and G13) are (22.7, 19.77, 18.08%), respectively when compared with control sample (G1). This enhancement is due carbon fiber has a high transverse strength, and also the surface treatment by immersing the carbon fiber in a PABA acid solution increased the formation of voids or pits on the surface of the fibers. This results in an increment in the fiber surface area, thus raising the strength of bond between the matrix and the fiber. Also, process of moistening fibers with the monomer before introducing them to the resin, this process strengthened the adhesion between fiber and resin. This improvement in flexural strength is attributed to the direction of the fibers, which means that the denture base polymer with woven carbon fibers is a very significant factor in orientation [28]. After coating the treated carbon fiber, F.S. is increased compared to control sample. The β-TCP coating was dense and firmly bonded to WCF, which enhanced the interface's physical bonding. The improved interconnection can efficiently transfer the load from the CF to the matrix. For the ceramic WCF reinforced, the fiber-matrix composites are the principal load-bearing, and therefore, the flexural strength is enhanced. It can be observed the optimal flexural strength was at (0.12 wi) of β-TCP. Moreover, the existence of (0.01 wi) of PVA in the reinforcement layer will cause to improve the flexural strength due to PVA has good tensile strength, high flexibility, and good hardness [25].

| Group no. | Flexural Strength (MPa) |
|----------|-------------------------|
| G4       | 82.35                   |

Table 5. The flexural strength for denture reinforced with woven carbon fiber.

4. Conclusion

Polymethyl methacrylate PMMA has successfully been reinforced with treated WCF by 0.10, 0.15, and 0.12 M of PABA and coated with 0.08, 0.10, and 0.12 wi of β-TCP. It can be concluded that the optimal acidic treatment for woven carbon fiber is (0.20 M) PABA concentration and the recommend weight fraction of β-TCP is (0.12 wi), which resulted 20.23 KJ/m² in impact strength test and 86.6 MPa in flexural strength test. This could be due to treated WCF with para-aminobenzoic acid improved the adhesion between fibers/ β-TCP powder and resin. Specimens of PMMA prepared by incorporation of β-TCP into woven carbon fiber have a good aesthetic. The results of the FTIR spectrum show the content
of oxygen functional was increased after acid treatment which leads to the enhancement of the mechanical properties of the fibers. The FESEM micrographs show that acid treatment increases the surface roughness of woven fibers.

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