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Research Article

Interfacial Adhesion and Physicomechanical Behaviours of Optimally Acetylated Kapok Fiber–Polymethylmethacrylate Composites for Prosthodontic Applications

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Special Issue
A Themed Issue in Honour of Professor Onukwuli Okechukwu Dominic (FAS).

This special issue is dedicated to Professor Onukwuli Okechukwu Dominic (FAS), marking his retirement and celebrating a remarkable career. His legacy of exemplary scholarship, mentorship, and commitment to advancing knowledge is commemorated in this collection of works.

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Interfacial Adhesion and Physicomechanical Behaviours of Optimally Acetylated Kapok Fiber–Polymethylmethacrylate Composites for Prosthodontic Applications

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Abstract

Interfacial adhesion and physicomechanical behaviours of optimally acetylated kapok fiber–polymethylmethacrylate (PMMA) composites for prosthodontic applications was investigated. Kapok fiber was extracted using water retting technique and chemically modified using acetic anhydride. The central composite design of response surface methodology (RSM) was employed to optimize the kapok fiber modification using 3-15 % of acetic anhydride and 30-150 minutes. Polymethyl methacrylate denture base material (95.25-99.25%) was modified with optimally acetylated kapok fiber (0.75-3.75%) and optimized based on tensile, flexural, hardness and impact properties. The density, water absorption and water absorption kinetics were determined. At optimum preparation of acetylated kapok fiber-PMMA, the tensile strength, hardness and interfacial adhesion were improved by 13.16, 8.06 and 67.93%, respectively, with reduced flexural strength (49.62%) and modulus (65.18%), and impact strength (22.52%). Acetylation reduced the density and water absorption of kapok fiber-PMMA by 8.6 and 117.53 %, restored the non-fickian water absorption behaviours and reduced coefficient. Hence optimized acetylated kapok fiber-PMMA denture base material enhanced the quality and durability with reduced residual monomer that may lead to cytotoxicity of oral cavity.

Keywords: Kapok fiber, acetylation, Polymethyl methalcrylate, interfacial adhesion, water absorption

1. Introduction

During setting of denture base material called polymethyl methacrylate (PMMA), high content of heat usually liberated which caused shrinkage and influenced the physical, mechanical and biocompatibility of the PMMA (Poornima et al., 2007). This means, the quality of denture base material (PMMA) depends on the tensile, flexural, impact and biodegradation couple with toxicity content of its monomer methylmethaacrylate (MMA). The interest of research community to improve the quality of PMMA via curing and copolymerization techniques of synthetic and natural materials has been an issue due to optimum issue performance. Clinical performance determined by

curing technique influenced physical and mechanical properties of PMMA. Plasma modification technique at low temperature altered the chemical composition, thereby, enhance surface energy, removal of impurities and weak surface formation of PMMA, with improved wettability and adhesion (Zhang et al., 2007). It has been revealed that water bath as a better favorable processing technique of PMMA material compared to microwave irradiation (Hassan et al, 2019; Badr et al, 2008). In the report of Ayaz et al (2013), the use of acrylamide monomer as copolymers increased the hardness of PMMA at glass transition temperature at variable content with no optimum composition.

The use of unsilanized and silanized glass fiber have been reported to enhance the tensile, flexural, hardness and impact properties of PMMA, but not at increased content of fiber. The enhanced properties were attributed to the lengthening of the polymer matrix chain (Ashwini, Veena & Swati, 2015; Oleiwi, Salih & Fadhil, 2018), but the expensive nature of glass fiber for prosthodontics remain a concern due to its production process (Nayar et al, 2015). PMMA modified with 5% nano-filler of zirconia (ZrO_2) increased the impact and transverse strengths with no significant difference in hardness and surface roughness (Ihab & Moudhaffar, 2011; Asopa et al, 2015). High content and short nature of nanofiller copolymerized with polymer matrix determine the shrinkage strain rate, thus improved mechanical properties of polymers (Garoushi et al., 2009). Many synthetic materials have been reported to be unsuccessful to improve the quality of PMMA due to absence of chemical bonding, difficulty of manipulation of PMMA, poor aesthetic, poor mechanical properties, poor aesthetics, high density and prone to brittle (Zafar, 2020). More so, the incorporation of dimethyl-2-dodecyl-1-methacryloxyethyl ammonium iodine (DDMAI), A19-Saponins and guava leaf extract remains promising techniques not only to prevent microbial deposition but to improve the mechanical and water sorption properties (He et al., 2013; Azeez et al, 2023; obiekwe et al, 2023). Water, an abundant saliva component which facilitate biodegradation through water molecules penetration into polymer network for the diffusion of unbound/uncured monomers called residue (MMA) (Bettencourt et al., 2010).

The water diffusion influenced by the water diffusion coefficient of PMMA based on saturation time and amount of residual components released and replaced by water molecules (Bettencourt et al., 2010). However, availability, light weight, inexpensive, hydrophobic, good relative mechanical and environmentally friendly properties of natural fibers, specifically plant fibers, such as *Cissus Populnea*, *Combretum Dolichopetalum*, breadfruit, roselle, avocado pear wood to mention a few have been used to reinforced the polymers (Sadeq et al, 2022; Azeez and Onukwuli, 2018a; 2018b; 2016). Chemically modification of these fibers using mercerization, acetylation, grafting, silanilization have been utilized to improve the performance polymers through improved interfacial adhesion (Government et al, 2021; Hameed & Ali, 2021; Azeez et al, 2020; Azeez and Onukwuli, 2018c; 2018d; 2017a; 2017b). Also, modification of natural fibers (wheat, barley legs, sisal, roselle, etc) have been reported to improve the quality of PMMA via increase in strength (Hameed and Ali, 2021), thermal and physical behaviours (Hameed et al, 2022), impact strength of sisal fiber modified PMMA composites (Okeke et al, 2018). The debonding of copolymers from PMMA resulted to physical and mechanical failures of the PMMA base composites which characterized by the adhesion of constituents, biofilm formation of *Candida albicans* and calculus. Modification of PMMA with soft liner coated silicone grafted with silane exhibited no increase in bond strength as reported (Atsü & Keskİn, 2013; Hamad, 2017). This is as a result of no molecular interaction and poor compatibility between the PMMA and fibers. More so, several plant fibers have been used to enhance the physical, mechanical and thermal properties of PMMA in prosthodontics with variation in aesthetics (colour) but kapok fiber with light brown and good hydrophobic natures are scarce in literature. In this work, the interfacial adhesion and physicomechanical behaviours of optimally acetylated kapok fiber-PMMA composites for prosthodontics as a rehabilitation engineering application was investigated.

2. Materials and Methods

2.1 Materials

Kapok *(Ceiba Pentandra)* plant stem was obtained from Gbana village in Ogbomoso, Oyo State, Nigeria and identified by Plant Biologist, Prof. A. T. J. Ogunkunle. Kapok fiber is a short fiber with Acetic anhydride (analytical grade chemicals) of more 98.5% purity, methylmethacylate (MMA) and polymethyl methacrylate (PMMA) of 99.9% purity were procured from Chemsciences Limited, Owerri, Nigeria.

2.2 Extraction, acetylation and optimization of kapok fiber

Kapok fiber was extracted from the plant stem via the water retting techniques in which plant stem was immersed in deionized water for 27 days, washed every 3 days, sun dried for 7 days and later oven dried at a temperature of 60^0C for 15 minutes. The length and diameter of kapok fiber was measured using measuring rule and digital vernier caliper, respectively, and then cutted into 120 mm. Kapok fiber was modified with acetic anhydride solution of varied concentration of 3-15% for 30-150 minutes at room temperature, washed, sun dried and then oven dried at temperature of 45^0C for 15 minutes. The tensile properties of kapok fiber were determined using universal tensile machine (Istron 3369 model) at a 4mm/min cross head speed with gauge length of 100 mm. The central composites design of response surface methodology (RSM) with quadratic model was employed for optimization as reported by Azeez and Onukwuli (2017).

2.3 Kapok fiber-PMMA composite preparation

Optimally acetylated kapok fiber (0.75-3.75wt % of the composites) and mixed manually with PMMA (99.25-96.25 wt%). Resin and fibers (1mm length) were mixed, the mixture was cast using hand laying method onto the dump bell cavity shape of a steel mold, previously coated with a mould releasing agent and allowed to cure.

2.4 Aspect ratio and density

Fibers were cut into a length of 100 cm at optimum conditions. The aspect ratio and density was determined before and after modification using equations (1) and (2), respectively, as described by Azeez et al (2017) respectively.

$$\rho_{kf} = \frac{M}{V} \quad (1)$$

$$A_{rk} = \frac{l_{kf}}{d_f} \quad (2)$$

Where $A_{rk}, d_f, M, V, \rho_{kf}$, and l_{kf} represent the aspect ratio, diameter, immersed weight, displaced volume, density and critical length of the kapok fiber, respectively.

2.5 Mechanical analysis of the kapok fiber-PMMA biocomposites

Tensile and 4-point flexural tests and standard dumb bell composite samples with a dimension of 80mm x 14mm x 6.4mm for kapok fiber-PMMA composites at test speed 40mm/min using universal testing machine (Instron 3369 model) at Engineering Development Institute, Akure . Unnotched Izod impact strength (I_s) was evaluated based on the energy absorbed using equation (3). Rockwell hardness was carried out at room temperature at Material and Metallurgical Laboratory, Federal University of Technology, Owerri, Nigeria in according with ASTM D – 785 using Rockwell hardness tester model Testor HT 1a, Otto Wolpert-Werke with steel indenter. Load of 150 kgf was applied on each sample with parallel flat surfaces placed on the apparatus and minor load (15 kgf) was applied to lower the steel ball on the sample surface. The dial was adjusted to zero on the scale under minor load and the major load (150 kgf) was applied via release of trip lever and then removed after 15 second. Rockwell hardness (HR) was read directly on the dial and recorded.

$$I_s = \int_0^D \frac{f\partial x}{ab} \quad (3)$$

The absorbed energy ($\int f\partial x$) by sample corresponds to the shaded area of a tensile plot. where *a* and *b* represent width and thickness of the biocomposites and *D* is the deflection at the fracture point.

2.6 Interfacial adhesion shear strength

The interfacial adhesion between PMMA with kapok fibers was determined using pull-out test under 0.4mm/min of cross-head speed of Instron Universal testing machine with applied load of 100kg. The PMMA composite was held in one end and pull out of fiber from the free end. The debonding load, P, and fiber diameter displaced were measured. Then, interfacial shear strength was evaluated by the equation (4) as described by Raj *et al* (2011):

$$\tau = \frac{P}{\pi dl} \quad (4)$$

Interfacial shear strength of biocomposites is τ, P is the debonding maximum pull-out force, d and l represent the diameter and length of the kapok fiber embedded in the PMMA matrix.

2.7 Water absorption and kinetics

Water absorption test was carried out in accordance with ASTM D 570 - 98. Prior to testing, kapok fiber-PMMA composites was oven dried at 60^0C for 6 hours and weighed. Kapok fiber-PMMA composites was immersed in deionized water and removed after every 10 minutes, wiped free of surface water and immediately weighed. The process was continued until water saturation was attained and the weight of the kapok fiber-PMMA composites was measured in triplicate with error weight error of ±0.5. Equation (5) was used to evaluate water sorption (Shah *et al*., 2012; Nguyen *et al*., 2012; Thiruchitrambalam *et al*., 2009):

$$Water\ sorption\ (W_s) = \frac{W_t - W_0}{W_0}\ x\ 100\% \quad (5)$$

W_t and W_0 represent the final weight of the kapok fiber-PMMA composites at time *t* and initial weight of the fibers, respectively.

The diffusion phenomenon was studied through water sorption method as described by Gierszewska-Drużyńska & Ostrowska-Czubenko (2012). The water diffusion mechanism through interphase based on the power law expression using equation (6) on a log-log (Azeez and Onukwuli, 2017).

$$\frac{M_t}{M_\mathrm{m}} = kt^n \quad (6)$$

Where M_t is the water content at specific time *t*, M_m is the water absorption at saturation point, and *k* and *n* are constants. The magnitude of *n* indicated whether the biocomposites is governed by Fickian diffusion model or non – Fickian diffusion model.

2.8 Fourier transform infrared (FTIR) and scanning electron microscope (SEM) analysis

Denture base material of 5.0g at optimal conditions was crushed into pellet and 0.1 g was mixed with 0.4g of dried potassium bromide (KBr), then transferred into sample compartment of Buck Scientific M500 Infrared Spectrophotometer. The spectrum was run with wavenumber range of 600 – 4000 cm^{-1} with scanning period of 20 seconds. The spectrophotometer was set at 100% transmittance with pure KBr pellet and the transmittance reading was obtained, stored and plotted. The absorption peak corroborates functional group. High resolution scanning electron microscope (SEM) of ASPEX 3020 model was used to study the morphology of the PMMA denture base material and its composites with unacetylated and acetylated kapok fiber. The PMMA denture base sample was examined directly by SEM with silver paste of a thin film of vacuum-evaporated platinum at 20 KeV and 5.0 $x10^{-5}$ torr before the photomicrographs or spectrum was taken.

3.0 Result and Discussion

The variation in tensile strength and modulus of acetylated kapok fiber based on central composite design (CCD) with increased concentration of acetic anhydride and time is presented in Table 1. Based on the data obtained, the quadratic models were suggested due to p-values of 0.0164 and less than 0.0001 inferior to (0.05) with high correlation coefficient (R^2) of 0.8161 and 0.9876 for tensile strength and modulus, respectively. This indicates 18.39 and 1.34% error which might be attributed to some factors that are put not into consideration during modification for tensile strength and modulus, respectively. Adequacy precision of 7.1421 and 21.4414, respectively, indicates tensile strength and modulus to error ratio greater than 4, hence optimally acetylated kapok fiber models can be used for any applications upon truncation of insignificant model terms (*c* and *t* for tensile strength; *c*, *t* and *ct* for tensile modulus) since $p > 0.05$, and resulted to equations (8) and (9), respectively.

Table 1: Tensile response of acetylated kapok fiber

S/N	*c* (%)	*t* (mins)	T_{sk} (MPa)	T_{mk} (MPa)
1	9.00	90.00	3.98451	24456.3
2	15.00	30.00	8.45602	1349.82
3	17.49	90.00	89.7695	3454.23
4	9.00	5.15	46.0434	637.316
5	3.00	150.00	10.2948	1983.23
6	3.00	30.00	47.178	8275.72
7	0.51	90.00	48.5933	859.314
8	15.00	150.00	40.3181	2736.84
9	9.00	174.85	74.5185	964.533

c, t, T_{sk}, and T_{mk} represent the concentration of acetic anhydride, modification time, tensile strength and tensile modulus of kapok fiber, respectively.

$$T_{sk} = 3.98451 + 23.9363ct + 24.7436c^2 + 20.29347t^2 \quad (8)$$

$$T_{mk} = 24456.3 - 10686.8c^2 - 11364.8t^2 \quad (9)$$

Table 2 depicts the tensile properties, aspect ratio, density and water absorption of unmodified and optimally acetylated kapok fiber. Based on the optimization, acetylation improved the tensile strength and modulus of kapok fiber by 55.72 and 336.75% upon truncation of insignificant model terms with $p > 0.05$ and resulted to equations (8) and (9), respectively. It can be deduced that acetylation increased the aspect ratio by 3.96% of unmodified kapok fiber, but reduced the density and water absorption by 2.8 and 42.96% of unmodified kapok fiber, respectively. The increase in aspect ratio can be attributed to amorphous (hemicelluloses, lignins, pectins and other impurities) removal on kapok fiber surfaces which caused an increase in rough surface topography and diameter (Joseph *et al*., 2000; Thiruchitrambalam *et al*., 2009; Zannen *et al*., 2014). This indicated that the decrease in density of acetylated kapok fibers may be due to removal of amorphous constituents and this not only make the kapok fibers to be lighter but rather make its application models to be lighter. This is in agreement with the report of Namessan *et al* (2012). The reduction in water absorption indicates reduction in hydrophilic nature of the fibers, hence the more the hydrophobicity of kapok fiber. Acetylation increased the hydrophobic nature of kapok fiber which may reduce the extent of delamination, hence improved durability and effectiveness of kapok fiber in making denture and other rehabilitative devices.

Table 2: Physicomechanical properties of unmodified and Optimally acetylated kapok fiber

Fiber sample	*C (%)*	*t (mins)*	*pH*	T_{sk} *(N/mm2)*	T_{mk} *(N/mm2)*	d_f *(mm)*	L_{fk} *(mm)*	A_{kr} *(mm/mm)*	ρ_{fk} *(g/cm^3)*	W_s *(%)*
E	0	0	7±0.1	34.2719	3001.2	0.105	100	952.381	0.500	330
E_{AC}	13.63	128.14	2.0±0.2	54.1221	13107.7	0.101	100	990.099	0.486	188.24

E represents kapok fiber and subscript AC means acetylation.

The mechanical responses based on weight fractions of kapok fiber and PMMA is presented in Table 3. It can be deduced that tensile strength and modulus, hardness and impact strength of the PMMA denture base composites varied based on acetylated kapok fiber. The variation in mechanical responses may be attributed to intermolecular compatibility and void formation. The quadratic models of the form: $Y_i = \beta_0 + \beta_1 W_f + \beta_2 W_p + \beta_3 W_f^2 + \beta_4 W_p^2 + \beta_5 W_f W_p$ was used for optimization models of the mechanical responses (tensile strength and modulus, hardness and impact strength) of the acetylated kapok-PMMA denture base composites.

Table 3: Mechanical responses of acetylated kapok fiber-PMMA composites

W_f (wt%)	W_p (wt%)	T_{sc} (N/mm^2)	T_{mc} (N/mm^2)	F_{sc} (N/mm^2)	F_{mc} (N/mm^2)	H_c (*BH*N)	I_{sc} (J/mm^2)
2.25	97.75	27.251	1170.6	50.064	1719.7	33	0.040722611
2.25	97.75	27.251	1170.6	50.064	1719.7	33	0.0407226
2.25	97.75	27.251	1170.6	50.064	1719.7	33	0.0407226
0.75	99.25	31.134	545.82	51.587	2028.9	25	0.079158897
3.75	99.25	19.726	817.19	41.237	2519.1	31	0.018784572
2.25	97.75	27.251	1170.6	50.064	1719.7	33	0.0407226
0.1287	97.75	20.019	641.53	33.072	1878.9	24	0.031437862
3.75	96.25	22.991	937.28	42.779	2724	30	0.023269231
0.75	96.25	30.469	647.91	52.102	2056.2	25	0.076924897
4.3713	97.75	24.519	1015.3	45.627	2914.2	33	0.025872261
2.25	97.75	27.251	1170.6	50.064	1719.7	33	0.0407226
2.25	95.6287	27.101	1147.6	50.011	1749.7	32	0.039876693
2.25	99.8713	26.503	1098.2	51.174	1826.9	32	0.038717214

W_f and W_p denoted for weight fraction of acetylated kapok fiber and PMMA denture base material. T_{sc}, T_{mc}, T_{sc}, T_{mc}, H_c, and I_{sc} represent the tensile strength, tensile modulus, flexural strength, flexural modulus, hardness and impact strength of the acetylated kapok fiber-PMMA denture base composites.

The ANOVA for tensile strength, tensile modulus, flexural strength, tensile modulus, hardness and impact strength models of unacetylated and acetylated kapok fiber – ACRYL composites are presented in Tables 4 and 5, respectively. It shows that the tensile strength response models for unacetylated and acetylated kapok fiber – PMMA composites, respectively, were significant and adequate for design applications due to inferior p-values of 0.05 with high magnitude of correlation coefficients (R^2 and adj. R^2) and adequate precision > 4. The high magnitude of R^2 greater than 0.8 indicates good correlation between the significant weight fractions of kapok fiber and PMMA as independent variables and each of mechanical property of kapok fiber-PMMA denture base material and high value of adj. $R^2 > 0.8$ implies a good correlation of mechanical property in case of addition independent variable. Upon truncation of insignificant model terms, the tensile strength, tensile modulus, flexural strength, flexural modulus, hardness and impact strength optimally unacetylated and acetylated kapok fiber-PMMA denture base composites resulted to equations (10) - (15) and equations (16) – (21), respectively. The magnitude of adequacy precision of mechanical properties for optimally acetylated kapok fiber-PMMA denture base composites was found to be more than that of corresponding unacetylated composites as presented in Tables 4 and 5. Based on the RSM models of the kapok fiber-PMMA composites, the optimal values of weight fraction of kapok fibers and PMMA matrix were obtained with mechanical properties. The choice of optimal values of mechanical properties for models was based on high desirability.

Optimized models for unacetylated kapok fiber-PMMA composites:

$$T_{sk} = -291.42 + 16.622W_f + 0.62967W_f^2 \quad (10)$$

$$T_{mk} = -45622.689 + 1240.651W_f + 948.471W_m - 230.914W_f^2 \quad (11)$$

$$F_{sk} = -7989.78698 + 163.91088W_m - 19.15267W_f^2 - 0.84W_m^2 \quad (12)$$

$$F_{mk} = -2107950.95 + 278.06W_f - 691.98W_f^2 \quad (13)$$

$$H_k = -1586.87 + 38.967W_f - 1.405W_f^2 + 0.3333W_fW_m \quad (14)$$

$$I_{sk} = -1.738 + 0.1041W_f - 0.00217W_f^2 \quad (15)$$

Optimized models for acetylated kapok fiber-PMMA composites:

$$T_{sk} = 1009.72957 - 15.33972W_m - 0.95392W_f^2 + 2.02475W_fW_m \quad (16)$$

$$T_{mk} = -102100 + 3003.3522W_f + 2080.6765W_m - 200.8978W_f^2 \quad (17)$$

$$F_{sk} = 1150.24 + 14.6795W_f - 1.512W_f^2 \quad (18)$$

$$F_{mk} = 239144.31 + 7276.67W_f + 162.166W_f^2 + 26.999W_m^2 - 79.215W_fW_m \quad (19)$$

$$H_k = -7100.588 - 49.2661W_f + 146.0881W_m - 1.0399W_f^2 - 0.7490W_m^2 + 0.5757W_fW_m \quad (20)$$

$$I_{sk} = -5.3229 + 0.0322W_f + 0.00495W_f^2 \quad (21)$$

Table 4: ANOVA for response surface quadratic models of mechanical responses of unacetylated kapok fiber-PMMA composites

Source	Model Coefficient	Sum of Squares	DF	Mean Square	F Value	Prob > F	R^2	Adj R^2	Adeq Precision
T_{sc}	-291.418712	186.60	5.00	37.32	52.2804	< 0.0001	0.9739	0.9553	22.8117
W_f	16.6219887	171.45	1.00	171.45	240.1730	< 0.0001			
W_p	6.14160928	0.62	1.00	0.62	0.8726	0.3813			
W_f^2	0.61966667	13.93	1.00	13.93	19.5194	0.0031			
W_p^2	-0.03044444	0.03	1.00	0.03	0.0457	0.8368			
W_fW_p	-0.167	0.56	1.00	0.56	0.7911	0.4033			
T_{mc}	-45622.6887	1.401E+06	5.00	2.802E+05	487.73	< 0.0001	0.9980	0.9959	5.6573
W_f	1240.65083	6.928E+05	1.00	6.928E+05	1205.84	< 0.0001			
W_p	948.47080	7761.36	1.00	7761.36	13.51	0.0144			
W_f^2	-230.91444	6.998E+05	1.00	6.998E+05	1218.05	< 0.0001			
W_p^2	-4.96667	713.60	1.00	713.60	1.24	0.3158			
W_fW_p	0.7766667	12.22	1.00	12.22	0.021	0.8898			
F_{sc}	-7989.78698	4929.43	5.00	985.89	5525.73	< 0.0001	0.9998	0.9996	14.7160
W_f	86.62417	0.70	1.00	0.70	3.95	0.1037			
W_p	163.91088	1.91	1.00	1.91	10.70	0.0222			
W_f^2	-19.15267	4906.41	1.00	4906.41	27499.58	< 0.0001			
W_p^2	-0.84	20.41	1.00	20.41	114.41	0.0001			
W_fW_p	-0.00733333	0.001089	1.00	0.001089	0.006104	0.9408			
F_{mc}	-2107950.95	20479068.74	5.00	4095813.75	7.7086	0.0091	0.8463	0.7365	8.0281
W_f	278.0614	2969833.77	1.00	2969833.77	5.5894	0.0500			
W_p	43240.5998	5084.65	1.00	5084.65	0.0096	0.9248			
W_f^2	-691.9806	15751732.68	1.00	15751732.68	29.6458	0.0010			
W_p^2	-221.6472	1730142.08	1.00	1730142.08	3.2562	0.1141			
W_fW_p	33.166667	22275.56	1.00	22275.56	0.0419	0.8436			
H_c	-1586.87199	54.33	5.00	10.87	48.6785	< 0.0001	0.9759	0.9559	19.3107
W_f	38.9668781	8.14	1.00	8.14	36.4865	0.0009			
W_p	32.2384336	0.02	1.00	0.02	0.0961	0.7671			
W_f^2	-1.40516073	43.06	1.00	43.06	192.9046	< 0.0001			
W_p^2	-0.16124272	0.85	1.00	0.85	3.8249	0.0983			
W_fW_p	-0.33333333	2.25	1.00	2.25	10.0802	0.0192			
I_{sc}	1.73756935	0.001645765	5.00	0.00032915	27.8320	0.0002	0.9521	0.9179	17.5579
W_f	0.10410151	0.001442387	1.00	0.00144239	121.9631	< 0.0001			
W_p	-0.0364196	1.40359E-05	1.00	1.4036E-05	1.1868	0.3120			
W_f^2	-0.0021699	0.000172596	1.00	0.0001726	14.5941	0.0065			
W_p^2	0.00019183	1.2959E-06	1.00	1.2959E-06	0.1096	0.7503			
W_fW_p	-0.00087351	1.54511E-05	1.00	1.5451E-05	1.3065	0.2906			

Table 5: ANOVA for response surface quadratic models of mechanical responses of acetylated kapok-PMMA composites

Source	Model Coefficient	Sum of Squares	DF	Mean Square	F Value	Prob > F	R^2	Adj R^2	Adeq Precision
T_{sc}	1009.72957	108.29	5.00	21.66	22.67	0.0008	0.9497	0.9078	14.671
W_f	-192.82414	3.32	1.00	3.32	3.48	0.1116			
W_p	-15.33972	9.96	1.00	9.96	10.43	0.0179			
W_f^2	-0.95392	44.45	1.00	44.45	46.53	0.0005			
W_p^2	0.05341	0.75	1.00	0.75	0.79	0.4097			
W_fW_p	2.02475	49.81	1.00	49.81	52.15	0.0004			
T_{mc}	-1.02E +05	6.208E+05	5.00	1.242E+05	48.02	0.0003	0.9796	0.9592	16.4680
W_f	3003.35222	38310.23	1.00	38310.23	14.82	0.0120			
W_p	2080.67649	26602.27	1.00	26602.27	10.29	0.0238			
W_f^2	-200.89778	5.439E+05	1.00	5.439E+05	210.35	<0.0001			
W_p^2	-10.60000	3250.41	1.00	3250.41	1.26	0.3131			
W_fW_p	-20.80889	8768.45	1.00	8768.45	3.39	0.1249			
F_{sc}	1150.23685	124.97	5.00	24.99	72.9614	0.0001	0.9865	0.9730	23.9434
W_f	14.6795278	96.76	1.00	96.76	282.4435	< 0.0001			
W_p	-22.737995	0.02	1.00	0.02	0.0620	0.8132			
W_f^2	-1.512	27.53	1.00	27.53	80.3670	0.0003			
W_p^2	0.1174444	0.40	1.00	0.40	1.1648	0.3298			
W_fW_p	-0.114111	0.26	1.00	0.26	0.7697	0.4205			
F_{mc}	239144.3052	2091896.43	5.00	418379.29	74.5938	< 0.0001	0.9842	0.9710	24.3202
W_f	7276.671149	1021685.49	1.00	1021685.49	182.1587	< 0.0001			
W_p	-5065.70224	16093.98	1.00	16093.98	2.8694	0.1412			
W_f^2	162.1656242	936718.86	1.00	936718.86	167.0098	< 0.0001			
W_p^2	26.99895752	41156.11	1.00	41156.11	7.3378	0.0352			
W_fW_p	-79.215281	76241.99	1.00	76241.99	13.5934	0.0102			
H_c	-7100.5883	141.41	5.00	28.28	124.11	< 0.0001	0.9920	0.9840	27.9880
W_f	-49.26609	77.18	1.00	77.18	338.68	< 0.0001			
W_p	146.08806	7.16	1.00	7.16	31.43	0.0025			
W_f^2	-1.03992	40.12	1.00	40.12	176.05	< 0.0001			
W_p^2	-0.74903	12.95	1.00	12.95	56.85	0.0006			
W_fW_p	0.57567	4.00	1.00	4.00	17.53	0.0086			
I_{sc}	-5.3228589	0.003759699	5.00	0.00075194	327.6715	< 0.0001	0.9964	0.9933	54.9513
W_f	0.0322139	0.003222209	1.00	0.00322221	1404.1362	< 0.0001			
W_p	0.10974934	1.89191E-06	1.00	1.8919E-06	0.8244	0.3989			
W_f^2	0.00494607	0.000514219	1.00	0.00051422	224.0801	< 0.0001			
W_p^2	-0.0005544	1.00946E-05	1.00	1.0095E-05	4.3989	0.0808			
W_fW_p	-0.0007465	1.12851E-05	1.00	1.1285E-05	4.9177	0.0684			

The optimal values of untreated and treated weight fraction of kapok fiber and PMMA matrix with the mechanical properties for predicted and experimental values are presented in Table 6. The predicted values for most mechanical properties are close to the experimentally validated values. The untreated kapok fiber increased the tensile strength, tensile modulus, flexural strength, flexural modulus, hardness with reduced impact strength of the PMMA composites. Acetylation improved the tensile strength, tensile modulus, flexural strength, flexural modulus, and hardness of kapok fiber-PMMA composites but reduced the impact strength. The increased tensile strength obtained when modified PMMA with unacetylated and acetylated kapok was found to more than twhen modified with nano zirconia nanofiller as reported by Ihab (2011). The increase in flexural strengths of unacetylated and acetylated kapok fiber-PMMA when compared to PMMA were found to be 223.07 and 61.14 %, respectively, which is more than that of mercerized roselle fiber (Okeke et al, 2018) and glass fiber reinforced PMMA (Ashwini et al, 2015) as well as the impact strength with mercerized roselle fiber, siwak powder and coconut shell powder (Okeke et al,

2018; Khalaf et al, 2013; Obiekwe et al, 2024). Also, acetylated kapok fiber increased hardness of PMMA more than nanofillers of zirconia (Ihab, 2011), reduced in the case of coconut shell powder (Obiekwe et al, 2024). Acetylation of kapok fiber reduced the quantity of PMMA which leads to reduction in MMA; hence minimized the toxicity that may arise by MMA (Azeez et al, 2023; Obiekwe et al, 2024). Table 7 reveals that acetylation of kapok fibers reduced the diameter of fibers, thereby, increases the interfacial adhesion of kapok fibers. This may be attributed to morphology of surface structure via removal of amorphous constituents.

Table 6: Optimal data of mechanical properties of kapok fiber - PMMA composites

Composite Sample	PMMA	PMMA+E	PMMA+E_{AC}
W_f	0	2.63	2.45
W_p	100	97.14	96.25
T_{sa}	20.152	24.084	27.253
T_{sp}	20.152	23.2413	27.5824
T_{ma}	515.9	1513.4	1089.32
T_{mp}	515.9	1509.66	1087.92
F_{sa}	30.828	98.595	49.677
F_{sp}	30.828	99.5701	49.532
F_{ma}	1754.4	5341.6	1859.68
F_{mp}	1754.4	5357.04	1867.03
H_a	24	31	33.5
H_p	24	30.8569	33.3293
I_a	0.187374	0.0463806	0.0359347
I_p	0.187374	0.0454989	0.0352877

Table 7: Evaluated interfacial shear stress of fiber-PMMA composites

Composite Sample	*F (N)*	d_f *(mm)*	*IFSS (N/mm^2)*
(PMMA+E)	868.50	0.105	2631.818
(PMMA+E_{AC})	1402.90	0.101	4419.577

Physical properties of PMMA composites

Table 8 depicts the physicomechanical behaviours of kapok fiber-PMMA denture base composites. Acetylation of kapok fiber reduced the density denture base composites by 8.06% of unacetylated kapok fiber–PMMA composites. Water absorption is an environmental condition associated with saliva which may affect the durability of the denture products, thereby, causes intercalation between the kapok fiber and PMMA. The water sorption of the composites refers to the strength of the composites to retain water which indicate the hydrophilic nature of the composites. This means, the lower the water sorption, the lesser the hydrophilic nature of the composites, the lesser the affinity for water and the more hydrophobic nature of composites which induced better durability of the composites. The acetylation of kapok fiber improved the water absorption of PMMA composites by 117.53% of unacetylated kapok fiber–PMMA composites. Based on Fickian diffusion model of equation (6) used, the value of n and k for PMMA composites was evaluated from Figure 1 and presented in Table 8. It can be deduced that water diffusion behaviours of PMMA denture base material matrix exhibits Non – Fickian since $0.5 < n < 1$ and incorporation of kapok fibers transient the water diffusion of the composites to Less Fickian behaviours since $n < 0.5$. This may be attributed to structural arrangement kapok fiber in PMMA as well as molecular interaction between the kapok fiber and matrix. Acetylation of kapok fiber restored the water diffusion mechanism of the composites to Non – Fickian behaviours since $0.5 < n < 1$ with reduced value of water absorption coefficient (k) at high value of correlation coefficient of $R^2 > 0.8$.

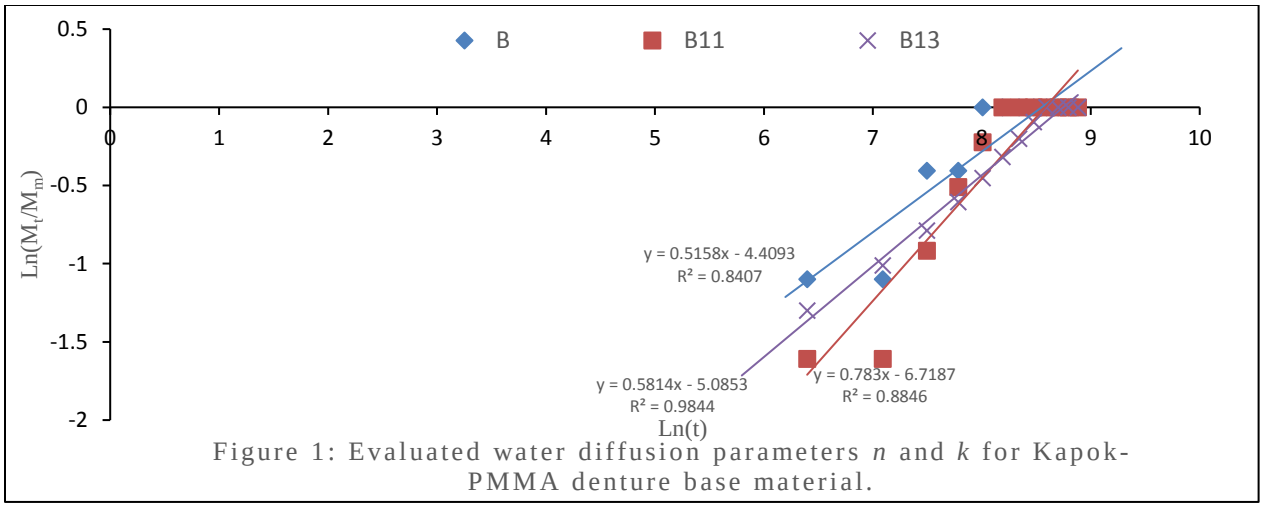

Figure 1: Evaluated water diffusion parameters *n* and *k* for Kapok-PMMA denture base material.

B, B11 and B13 represent PMMA, unacetylated kapok fiber-PMMA and acetylated kapok fiber-PMMA, respectively.

Table 8: Physical properties of PMMA composites

Composite Sample	W_f (%)	W_p (%)	ρ (g/cm^3)	h_c (mm)	n (s^{-1})	k	M_m (%)
PMMA	0	100	1.1618	4.4	0.5158	0.01216	0.3797
PMMA+E	2.67	97.18	1.236	4.4	0.783	0.00121	0.8091
PMMA+E_{AC}	2.70	96.25	1.1364	4.4	0.5814	0.00619	1.76

Functional groups and morphology of denture base material composites

Figure 2(a)-(c) depicts the functional groups in the PMMA matrix, unacetylated kapok fiber- PMMA and acetylated kapok fiber-PMMA, respectively. The unacetylated kapok fiber caused disappearance of C-H = C - H and C - H (bend) of alkenes with shift in absorption peaks of some functional groups as shown Figure 2(b) compared with PMMA denture base matrix (Figure 2(a)). The change in absorbance peaks and intensity of corroborates some functional groups. The disappearance and change in absorbance peaks couple with change in intensity may be attributed to removal of amorphous constituents (lignin and hemicellulose) present in the kapok fiber and molecular interaction between the unacetylated and acetylated kapok fiber and PMMA which resulted to change in mechanical properties of the composites.

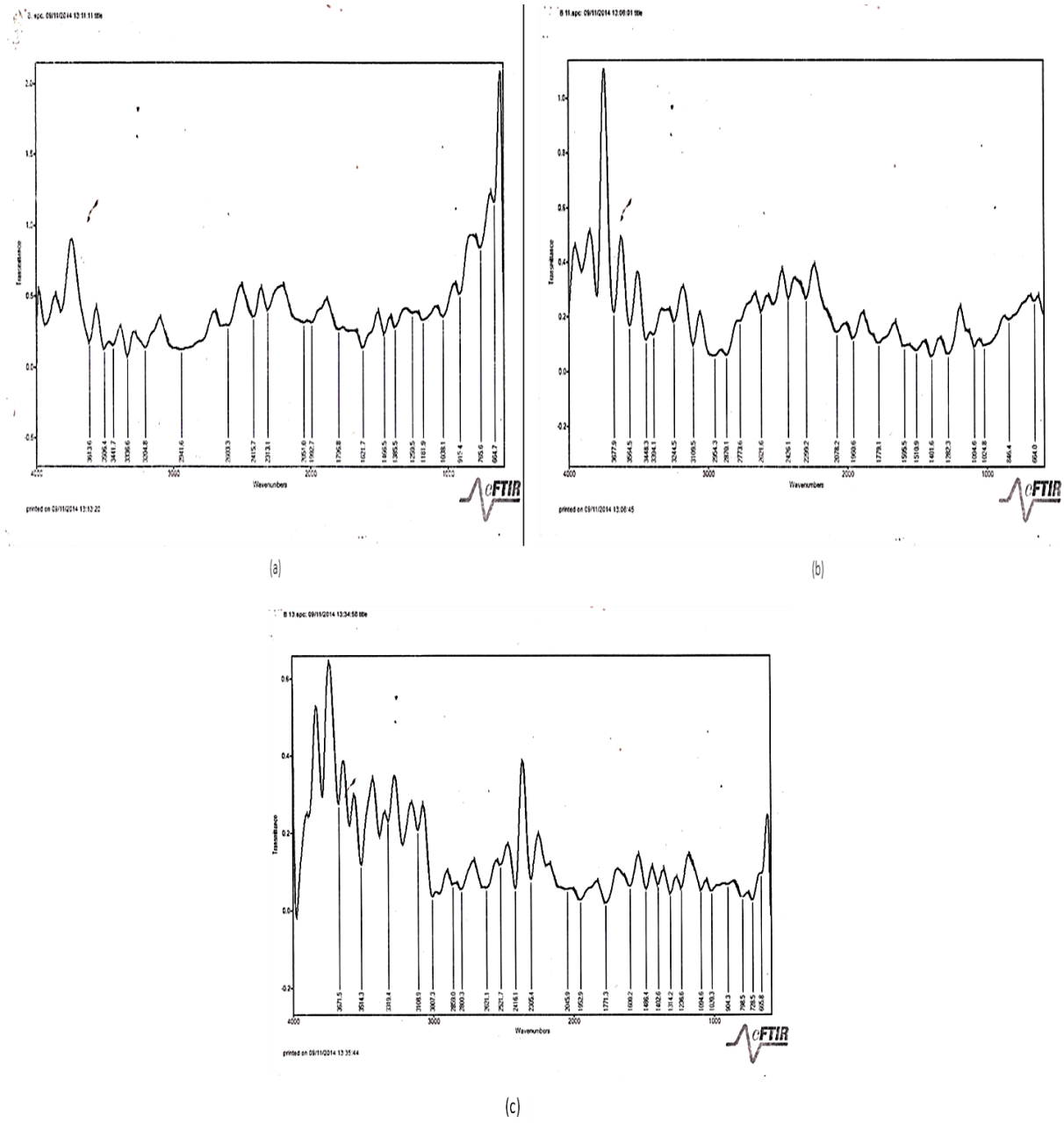

Figure 2: FTIR spectra of PMMA denture base material: (a) PMMA matrix (b) unacetylated kapok fiber - PMMA (c) acetylated kapok fiber –PMMA.

Figure 3(a)-(c) revealed the morphological changes by SEM micrographs in PMMA matrix, untreated and treated kapok fiber-PMMA denture base material, respectively. Figure 3(a) revealed homogeneous surface of the PMMA base matrix with micropores which leads to crack. Figure 3(b) unacetylated kapok fiber – PMMA failures include fiber breakage, tearing and debonding during stress transfer. Failures characterized by poor interaction between kapok fiber and PMMA, void formation, uneven distribution and fiber agglomeration. Acetylated kapok fiber improved the interfacial adhesion region between the fiber and PMMA as shown in Figure 3(c).

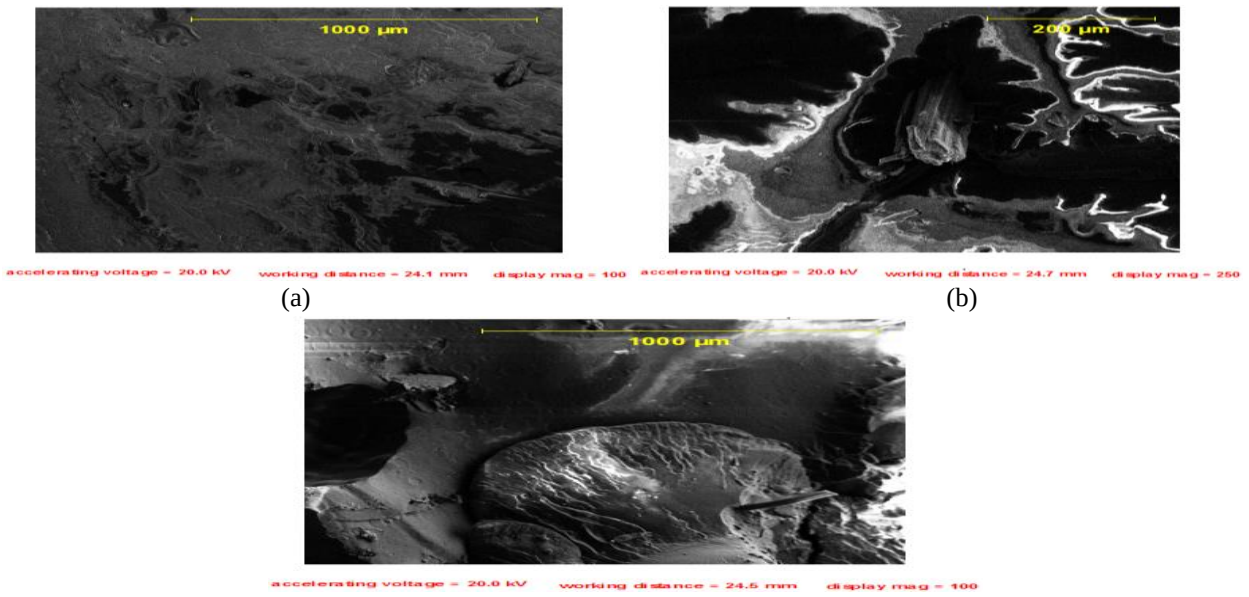

Figure 3: SEM of PMMA denture base: (a) PMMA matrix (b) unacetylated kapok fiber - PMMA (c) acetylated kapok fiber–PMMA.

4.0. Conclusion

Acetylation improved the tensile, flexural and hardness properties of kapok fiber-PMMA denture base material with reduced impact strength as well as interfacial adhesion between the kapok fiber and PMMA with reduced content of toxicity of methylmethacrylate. Optimally acetylation of kapok fiber reduced the density, water absorption and hydrophilic nature of the PMMA composites. The improvement in physicomechanical properties corroborates with interfacial adhesion between the acetylated kapok fiber and PMMA denture base material as also revealed by FTIR and SEM. Hence acetylated kapok fiber could use as alternative for glass fiber in prosthodontics applications like denture implant.

5.0 Recommendation

Based on this study, the use of unacetylated and acetylated kapok fiber is recommended as alternate to glass fiber in prosthodontics application and further research should be carried out to improve the performance on PMMA and other polymeric materials for domestic and industrial applications.

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Nomenclature

PMMA = Polymethyl methacrylate;
MMA = Methyl methacrylate;
C = Concentration of the acetic anhydride;
t = Treatment time;
E= kapok fiber;
E_{AC} = acetylated kapok fiber;

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