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Mechanical, biological, and characterization of nanoparticle-reinforced polyurethane for clear orthodontic aligners

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In the present work, the performance of polyurethane is enhanced through reinforcement with fluorapatite nanoparticles to develop a nanocomposite material suitable for advanced orthodontic applications. Fluorapatite nanoparticles with an average size of 53.5 nm are incorporated into the PU matrix at four different weight fractions (0.1, 0.2, 0.3, and 0.4 wt.%). The structural characteristics and interfacial interactions are examined using Fourier Transform Infrared Spectroscopy (FTIR), while the dispersion state of the nanoparticles is evaluated by Scanning Electron Microscopy (SEM). The results demonstrated that low nanoparticle loadings led to a uniform distribution within the polymer matrix, effectively minimizing agglomeration. Mechanical testing showed a marked improvement in hardness, increasing from 72 Shore D for pristine PU to 85 Shore D after nanoparticle reinforcement. Moreover, tensile strength exhibited a steady increase from 45 MPa in neat PU to 93 MPa at the highest nanoparticle concentration. These improvements are associated with enhanced interfacial bonding, reduced polymer chain mobility, and efficient load transfer across the nanocomposite structure. Biological performance assessment revealed an increase in antibacterial activity with increasing nanoparticle content, while all nanocomposite samples maintained acceptable biocompatibility. The findings confirm that fluorapatite-reinforced polyurethane nanocomposites possess improved mechanical strength and biological functionality, making them a promising material for next-generation clear dental aligners.

Keywords: Polyurethane; Nanofluorapatite; SEM; FTIR; Mechanical.

1. INTRODUCTION

The popularity of the use of clear aligners over the tradition metallic orthodontic braces has been remarkable in terms of their aesthetic outlook, comfort, and the ease of their extraction during day-to-day activities like eating and oral care routines. Clear aligners, unlike conventional fixed appliances, offer an orthodontic solution that is more discrete and patient-friendly as well as enabling better compliance to patients and overall satisfaction with the treatment. Clear aligners, which are usually made of thermoplastic polymers, including polyurethane (PU) or polyethylene terephthalate glycol (PET-G) need a fine balance of mechanical stability, sufficient elasticity, dimensional stability and high optical transparency to disclose controlled orthodontic forces during the treatment period in order to achieve effective and non-invasive orthodontic therapy [1-4]. Regardless of these benefits, the traditional materials employed in clear aligners frequently have a number of drawbacks, including the progressive decrease of mechanical characteristics in oral environment, exposure to discoloration and staining, and insufficient wear resistance with the long-term usage. Such obstacles have the potential to undermine the effectiveness and performance of aligner therapy over the long term. In such a way, the recent research works have aimed at enhancing the functional performance of aligner materials by integrating nanotechnology-based strategies [5–8]. Due to their high surface area to volume ratio, tunable physicochemical characteristics, and high interfacial compatibility with polymer matrices, nanoparticles have been shown to exhibit considerable promise in the area of improving mechanical strength, thermal stability, and optical characteristics of dental materials [9-13]. The treatment of orthodontics has experienced significant innovations over the past few years with the evolution of clear aligner systems which have been a significant innovation in not only the aesthetics but also the level of comfort as well as efficiency in treating patients. One of such systems, Invisalign, has become one of the most well-known and widely clinically used aligner systems, offering an alternative to conventional fixed orthodontic appliances in the form of a removable and almost invisible device. Unlike the conventional braces which are made of metallic brackets and archwires, clear aligners are made out of transparent thermoplastic polymers and are designed with a high level of digital modeling and manufacturing capabilities to exert exact and restrained forces. These forces allow achieving slow, controlled tooth movement without causing much pain or other unwanted side effects, which makes clear aligner therapy an even more popular choice in the contemporary orthodontic treatment. [14–16].

The performance and effectiveness of clear aligners are strongly determined by the intrinsic properties of the materials used in their fabrication. Ideal aligner materials must achieve a delicate balance between several critical factors, including mechanical strength, elastic recovery, optical clarity, biocompatibility, and resistance to thermal and chemical degradation. Among the thermoplastic polymers, thermoplastic polyurethane (TPU) has emerged as one of the most widely employed materials due to its unique combination of flexibility, toughness, and dimensional stability, making it well-suited for prolonged intraoral use [17–18]. Recent research has highlighted the potential of enhancing the properties of clear aligners through the incorporation of nanoparticles, such as silver (Ag) and titanium dioxide (TiO_2). These nanoparticles can contribute to improvements in mechanical strength, optical transparency, and antimicrobial activity, thereby increasing both the functional performance and biological safety of the aligners. Nevertheless, a comprehensive evaluation of the impact of such nanoparticle reinforcement on material characterization, including surface morphology, optical behavior, and long-term stability, is essential to ensure their safe and effective application in clinical practice [19].

Clearly, aligners have revolutionized the orthodontic treatment in that they offer an alternative method of orthodontic treatment that is less visible, comfortable and easily removable as opposed to the metallic braces. The increasing need of dentistry beauty solutions has led to wide research in the direction of optimization of the materials applied in aligner make. Majority of the commercial clear

aligners are made of thermoplastic polymers, namely polyurethane (PU), polyethylene terephthalate glycol (PET-G), polycarbonate (PC), which is highly appreciated due to its flexibility, transparency and biocompatibility. Nevertheless, all these advantages are accompanied by wear, discoloration, and mechanical deterioration of these polymers with time, especially in the harsh conditions of the oral cavity, in contact with saliva, temperature changes, and masticatory forces (Boyd, 2017 [20]; Kravitz et al., 2009 [21]). In an attempt to overcome the short-comings of traditional thermoplastic polymers in clear aligners, scientists have looked into the process of reinforcing polymer matrices with nanoparticles in order to improve the mechanical performance and optical properties of the polymer without affecting biocompatibility. The special benefits of nanoparticles are due to their high surface-volume ratio, their adjustable surface chemistry, and the possibility to alter the physical and mechanical behavior of the host polymer (Mohan et al., 2020) [22]. Dental composites have also extensively employed nanoparticles because they have the capacity to enhance tensile strength, hardness, wear resistance and dimensional stability. Nanoparticles when well distributed in polymer matrices can form a more rigid framework and help to implement UV protection, which can contribute to the higher resistance of the material to intraoral conditions (Chen et al., 2018) [23]. Of the above, titanium dioxide (TiO_2) nanoparticles are most preferred due to their high refractive index and excellent UV resistance that can be used in transparent and resilient dental materials. Nevertheless, overloading of nanoparticles or agglomeration may cause higher scattering of light, which causes low optical clarity and aesthetic quality. (Lohbauer et al., 2013) [24]. Nanoparticle reinforced polymers require thorough characterization to maximize their performance. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectrophotometry (FTIR) X-ray Diffraction (XRD) and UV-Visible (UV-Vis) spectrophotometry are some of the techniques that have been invaluable in assessing nanoparticle dispersion, surface functionalization, structural integrity, and optical behavior. Research studies conducted by Li et al. (2021) and Hasan et al. (2022) [26] revealed that homogeneous distribution of the nanoparticles and appropriate surface modification is essential to maximize mechanical reinforcement and minimize the negative impact on optical transparency. Moreover, mechanical tests have shown that nanoparticles in low concentrations (usually less than 0.4 wt) can improve the strength and stiffness of clear aligner materials without having a major impact on transparency. Contrary to this, nanoparticle loadings can be increased to the threshold where agglomeration occurs and results in light scattering, small changes of transmittance, and enhanced brittle character of the polymer mesh (Liu et al., 2019) [27]. These results indicate the fine line that needs to be maintained between the content of nanoparticles, mechanical improvement, and maintenance of optical and aesthetic features in clear aligners. Although the results of in vitro experiments indicate the potential expected advantages of nanoparticle reinforcement, there is massive gap in long-term clinical study to assess the performance of nanoparticle-enhanced clear aligners in actual intraoral conditions. The majority of available literature is mainly interested in short-term characterization including mechanical strength, hardness, or optical properties, and long-term impacts on durability, biological safety, and clinical efficacy are not researched extensively. Thus, the research in the future would incorporate both short-term material tests and longitudinal clinical tests to give the overall picture on the performance of nanoparticle-modified aligners. The main aim of the research is to investigate the effect of the use of sustainably sourced nanoparticles in the mechanical, structural, and functional characteristics of clear aligner materials. Through the systematic research on the various types of nanoparticles, loads, and dispersion techniques, this study will attempt to establish some of the best nanoparticle compositions that will improve the material performance without compromising on biocompatibility, optical transparency, and structural integrity. Rational material design and enhancement of clinical outcomes will be facilitated by comparative analyses of the mechanical, chemical, and biological properties.

Although aesthetically beneficial and friendly to patients, there exist inherent mechanical and chemical constraints to clear aligners, which could impair their clinical actions in the long run. Thermoplastic polymers, i.e. polyurethane (PU), polyethylene terephthalate glycol (PET-G) and polycarbonate (PC)

are also susceptible to deformation, stress relaxation, and slow decrease in the provision of forces with time. The results are increased in terms of cyclic masticatory loading, changes in intraoral temperature, and repetitive processes of insertion/removal, which results in reduced orthodontic forces, inaccurate movement of teeth, and possible delays in treatment. Other mechanical difficulties comprise wear of surfaces, micro-cracking and the lack of resistance to high tensile or flexural stresses especially in patients who show parafunctional behaviors like bruxism or clenching.

Chemically, clear aligners are prone to hydrolytic, saliva components sorption, and polymer chain changes in response to acidic, enzyme, or changing pH environment in the mouth. The chemical reactions may lead to loss of transparency and decreased stiffness and loss of dimensional stability, which in addition to aesthetic effect diminish predictability of orthodontic treatment. Besides, long-term exposure to oral cavity may provoke the loss of residual monomers, plasticizers, or other additives, which is a concern in terms of long-term biocompatibility and cytotoxicity. Mechanical fatigue and chemical instability can be seen as a reminder of the fundamental urgency to develop new material formulations that will enable the enhancement of the clear aligner systems in terms of their stability, reliability, and safety [28]. In this regard, the integration of nanomaterials is an attractive approach since they have remarkably large surface-to-volume ratio, tunable surface chemistry and are capable of reinforcing polymer matrices in a more efficient manner compared to traditional micro-sized fillers. Nanoparticles have the ability to increase mechanical properties, wear resistance, and UV stability concurrently, and can also offer antimicrobial activity and optical transparency, hence overcoming several drawbacks of conventional aligner materials. This experiment, hence, aims at critically assessing the mechanical, structural and biological properties of nanoparticle-reinforced aligners with the view to setting standards on designing the next generation orthodontic materials [29-33].

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Polyurethane (PU) is a man-made synthetic polymer created by a polyaddition reaction of polyols and isocyanates, to create a material that has extremely adjustable mechanical, physical, and chemical characteristics. Because of this range of use, PU has found wide use in biomedical applications, especially in orthodontics, where it is needed to be able to control elasticity, optical transparency and biocompatibility. In this research PU is chosen as the starting polymer in the production of clear dental aligners due to its high transparency, elasticity, biocompatibility, and the ability to provide long-acting orthodontic forces. The reinforcing fillers incorporated to improve the performance of the polyurethane matrix are the fluorapatite nanoparticles with the average size of 53.5 nm. The concentration of nanoparticles used is varied to four powder loadings (0.1, 0.2, 0.3, and 0.4 wt.%) to determine the influence of concentration on the structural and functional characteristics of the nanocomposites formed. The fluorapatite nanoparticles are surface modified before they are incorporated in the PU matrix in order to enhance their dispersion and compatibility with the polymer.

The nanoparticles are spread into ethanol and subjected to 30 minutes ultrasonication with 40 kHz frequency. This is done to properly hinder nanoparticle agglomerates, enhance homogeneous dispersion and the homogeneous distribution of the nanoparticles throughout the polyurethane matrix. This type of treatment is essential in reducing particle clustering, and improving interfacial adhesion between filler and polymer matrix and maintenance of optical clarity, as well as mechanical integrity of the end result nanocomposite material.

2.2 Material strength characteristics
2.2.1 Micro-scale hardness test

They are tested using the Shore hardness test to check the hardness of the polymeric materials. Each formulation is tested on 5 specimens with a size of 1 cm by exerting a standardized indenter force. The hardness value is directly measured using a Shore durometer and the resistance of the material to indentation is measured and the value recorded. In the case of the thermoplastic polyurethane samples, the Shore D scale is chosen because it is applicable to materials with a relatively increased level of stiffness. The test is fast, non-destructive, and simple to carry out and thus suitable in the characterization of material and quality control of polymer-based nanocomposites.

2.2.2 Tensile strength

Tensile property of the prepared specimens is determined as per ASTM D638 whereby five tensile specimens in each material formulation are prepared and tested to make the results repeatable and reliable. All the tests are conducted in a universal testing machine (UTM) that had a load cell capacity of 50-100 N. The test is conducted under the same conditions of 2 mm/min of crosshead speed to maintain homogenous conditions in the deformation. When tensile loading is done stress strain data are recorded continuously and the stress strain curve are plotted. The following curves are then determined in order to derive the important tensile parameters which are the tensile modulus, strain at failure (elongation at break) and ultimate tensile strength (UTS). The tensile test will give the necessary information concerning the mechanical characteristics of the polyurethane-based nanocomposites and the effects of the addition of nanoparticles on the load-bearing stress and deformation properties of the nanocomposites.

2.3 Morphological and structural characterization
2.3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is employed to identify the characteristic functional groups of the polyurethane matrix and to investigate possible chemical interactions between the polymer and the incorporated nanoparticles. FTIR spectra are recorded for five representative aligner material samples for each formulation using an FTIR spectrometer within the wavenumber range of 600–4000 cm^{-1}. The obtained spectra are analyzed using specialized FTIR software to detect changes in peak positions, intensities, or the appearance of new absorption bands, which may indicate interfacial interactions or bonding between the polymer matrix and nanoparticles.

2.3.2 Field emission scan electrons microscopy (FESEM)

The surface morphology and microstructural features of the prepared polyurethane-based nanocomposites are examined with the help of Field Emission Scanning Electron Microscopy (FESEM). Each formulation had five samples to represent them in the analysis. In FESEM analysis, high-energy electron beam is focused on the surface of the sample to produce several kinds of signals including secondary and backscattered electrons. These signals are measured by detecting the signal in the microscope and are able to tell in great detail the topography of the surface, the state of dispersion of the nanoparticles, and the location of agglomerations in the polymer matrix.

Due to its high resolution, great magnification, and level of analysis, FESEM permits a detailed analysis of a vast surface area at the micro- and nanoscale. The method is especially useful in assessing nanoparticle location, interfacial adhesion, and morphological homogeneity which are essential determinants of mechanical and optical performance of clear aligners materials.

2.4 Biological properties
2.4.1 Antibacterial test

The antibacterial activity of the polyurethane-based composite materials is evaluated by assessing their ability to inhibit bacterial adhesion and biofilm formation on the material surface. Biofilm formation refers to the accumulation and growth of bacterial cells on solid, non-living surfaces, which represents a critical factor in biomedical applications such as clear dental aligners. In this study, five specimens with dimensions of 1 cm are prepared for each formulation, as illustrated in Figure 1 and Figure 2.

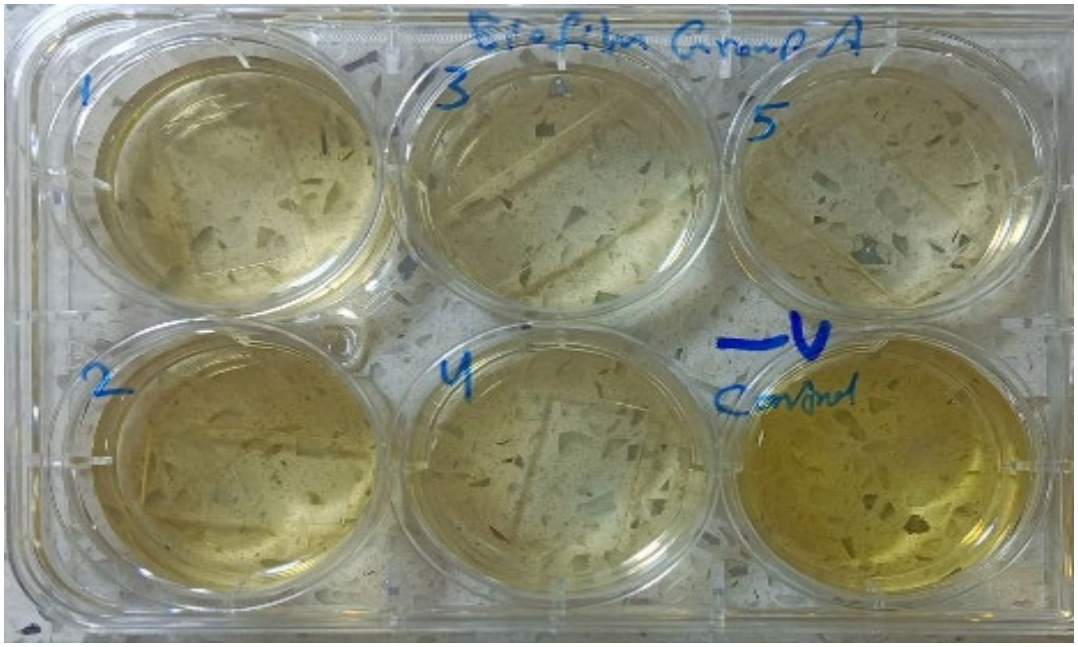

Figure 1 Six wells plate showing biofilm assay for all samples.

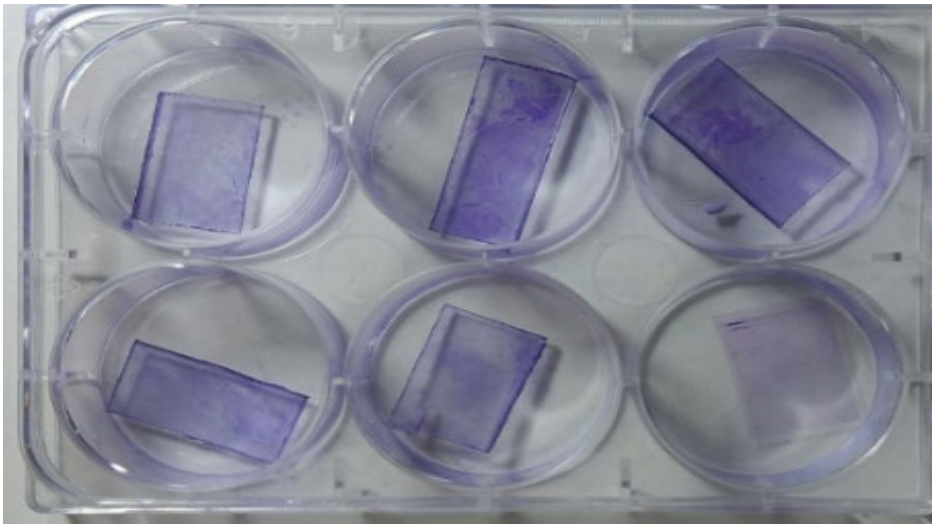

Figure 2 Biofilm assay after crystal violet using

The following are the steps followed to perform the antibacterial test against Staphylococcus aureus (Gram-positive bacteria) by the use of biofilm formation assay:

To prepare the samples, firstly the sample surfaces are washed with crystal violet solution that is applied to the surface of the sample to stain bacterial cells that attached to the surface. This is followed by the qualitative examination of bacterial aggregates and biofilm formation on the composite surfaces by observing them under a microscope. Second, in order to measure the bacterial adhesion quantitatively, a smear of the bacteria that built up on the surface of the polymer composite samples is prepared. The slide is put on a glass slide and observed using an optical microscope so as to determine the density and distribution of the bacteria cells. Third, ethanol is used to remove the biofilm layer on the sample surfaces and the optical absorbance of the obtained solution is determined with the help of the microtiter plate reader. The biofilm density is calculated by the absorbance values and the percentage of biofilm removal or inhibition is calculated by using Equation 1.

$$Biofilm\ Inhibition\ (\%) = \left(\frac{Control\ OD_{630\ nm} - Treated\ OD_{630\ nm}}{Control\ OD_{630\ nm}}\right) \times 100 \quad (1)$$

Several materials are used in the course of this experiment: polystyrene 6-well and 96-well plates, 22 x 22 mm glass cover slips, ethanol solutions with 70 and 95 percent of glucose, phosphate-buffered saline (PBS), brain heart infusion (BHI) broth culture medium, 2 percent of glucose solution, filtered, crystal violet solution, normal saline and 0.5 McFarland standard. The experimental protocols are conducted through the use of an autoclave to achieve sterilization, the use of an incubator to help culture the bacteria, the use of a microtiter plate reader to measure the absorbance of the bacterial culture as well as the use of an optical microscope to observe the bacteria.

2.4.2 Cytotoxicity test by hemolytic assay

To determine the cytotoxicity of the prepared materials, the hemolytic assay is used, which is an established procedure used to determine the impact of materials on the integrity of cell membranes. The principle of the given assay is assessing the aptitude of potentially harmful substances to destabilize the membranes of cells and impair their ability to hold intracellular constituents. It is regarded as one of the most important preliminary techniques of finding cytotoxic effects, especially on the case of biomedical materials to be in contact with blood or biological fluids.

The hemolytic assay in this research is particularly applied in order to investigate the interaction of the fabricated polymeric composites with the human erythrocytes (red blood cells) in vitro. The test gives a clue on the level of toxicity of the materials on the blood cells by measuring the amount of hemoglobin that is released due to the damage of the erythrocyte membranes. Such an evaluation is used as the first screening measure to determine the safety or potential danger of the materials used in biomedical use, particularly when in contact with blood tissue fluids or in relatively high concentrations. The principle of hemolytic assay is based on the fact that cytotoxic substances have the capacity of rupturing the membranes of the erythrocyte, which results in the release of intracellular hemoglobin into the surrounding medium. Quantitative cytotoxicity is then assessed by quantitatively measuring concentration of released hemoglobin by spectrophotometric analysis.

The test process is carried out in two processes. To begin with, the quantity of hemoglobin that is released due to red blood cell hemolysis is spectrophotometrically determined. Second, the erythrocytes morphology is observed with the help of an optical microscope and compared to the negative control (the phosphate-buffered saline, PBS), which is a sample of non-hemolyzed and normal erythrocytes, and the positive control, which is the full hemolysis of the red blood cells. Equation is used to calculate the hemolysis ratio (HR %). (2).

$$Hemolysis\ Ratio\ (HR\%) = \frac{[OD_{test} - OD_{negative\ control}]}{[OD_{positive\ control} - OD_{negative\ control}]} \times 100\% \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Morphological and structural analysis

3.1.1 Spectroscopy (FTIR) analysis

FTIR spectra of five specimens of clear polyurethane (PU) that had been reinforced with nanofluroaptite to make dental aligners are examined to determine the chemical structure and potential interactions of the polymer matrix and the nanoparticles. Figure 3. Polyurethane matrix and the fluorapatite nanoparticles represented by analytical FTIR. The spectra indicate typical absorption bands which are related to the polyurethane matrix and filler of nano-silica, which further indicates successful incorporation of the nanomaterial without modifying the major chemical structure of the polymer.

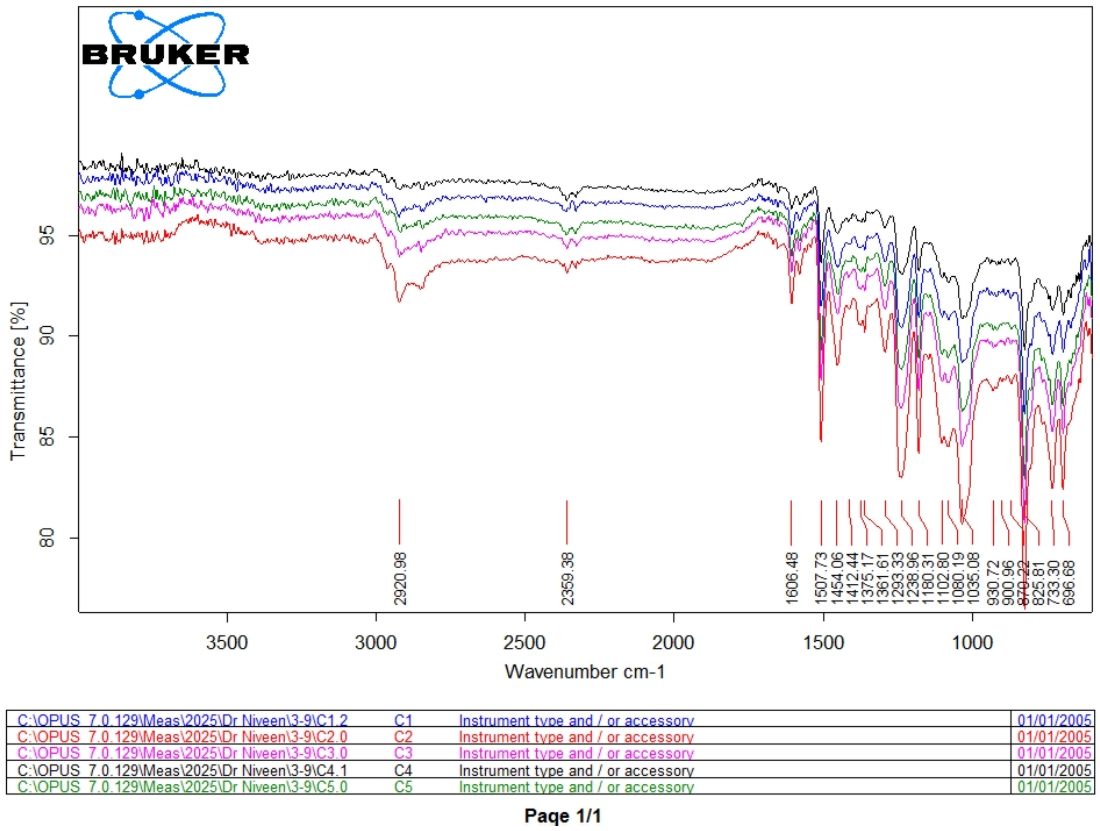

Figure 3 FTIR spectrum of polyurethane reinforced with nano- fluorapatite.

The FTIR spectroscopy of the polyurethane (PU) matrix reinforced by fluorapatite nanoparticles (n-FAp) at various loading (0.1, 0.2, 0.3 and 0.4 wt.%) can provide valuable information on the interfacial interaction between the polymer and the inorganic phase. The typical absorption bands of PU are evident in the entire sample and contained the C-H stretching vibrations of around 2920 and 2850 cm^{-1}, the carbonyl (C=O) stretching band of the urethane group at approximately 1700-1650 cm^{-1} and the N-H bending and C-N stretching vibrations at around 1530 cm^{-1}. When n-FAp is incorporated, there is a gradual decrease in the intensity and slight shift of the C=O and N-H related bands that showed the occurrence of intermolecular hydrogen bonding between the functional groups of PU and Ca^{3+}, PO_4-groups of fluorapatite. In addition, the formation and gradual increase of absorption bands at 1100-

1000 cm^{-1} and 960-560 cm^{-1}, which is attributed to the stretching vibration and bending vibration of PO4 - groups, testify to the effective incorporation and even distribution of n-FAp in the PU scaffold. Notably, no further peaks or radical differences in the spectrum indicate that the chemical structure of the PU is disrupted due to the addition of the nanoparticle, which also means that the process of reinforcement is more physical-based. This good interfacial interaction is likely to improve the mechanical behavior and bioactivity of the composite and still maintain its optical transparency. Table 1. Illustrated Characteristic peaks of polyurethane matrix and the fluorapatite nanoparticles.

Table 1 Characteristic peaks of polyurethane matrix and the fluorapatite nanoparticles.

Wavenumber (cm^{-1})	Functional Group / Peak Assignment	Explanation
2920–2850	C–H stretching (CH_2 / CH_3)	Represents the asymmetric and symmetric stretching vibrations of aliphatic C–H bonds in the polyurethane backbone. Minor intensity reduction after nanoparticle addition indicates restricted polymer chain mobility due to nanoparticle incorporation.
1700–1650	C=O stretching (urethane carbonyl)	Characteristic of the urethane linkage in PU. The slight shift and decreased intensity with increasing n-FAp content suggest hydrogen bonding interactions between the PU carbonyl groups and Ca^{2+} or PO_4^{3-} ions of fluorapatite nanoparticles.
1530–1510	N–H bending and C–N stretching (Amide II)	Associated with urethane groups. Changes in peak intensity indicate physical interactions and interfacial bonding between PU chains and n-FAp particles.
1450–1370	CH_2 bending vibrations	Corresponds to deformation vibrations of aliphatic chains in PU. The presence of nanoparticles slightly alters peak intensity due to polymer chain confinement.
1250–1220	C–N stretching (urethane linkage)	Confirms the integrity of the polyurethane structure after nanoparticle reinforcement, with no evidence of chemical degradation.
1100–1000	PO_4^{3-} stretching vibrations	Characteristic bands of fluorapatite nanoparticles. The progressive increase in intensity with higher n-FAp loadings confirms successful incorporation and increasing nanoparticle content within the PU matrix.
~960	PO_4^{3-} symmetric stretching	Indicative of the crystalline phosphate structure of fluorapatite, becoming more pronounced at higher nanoparticle concentrations.
600–560	PO_4^{3-} bending vibrations	Further confirms the presence of fluorapatite nanoparticles and their stable dispersion within the polymer matrix.

3.1.2 Scanning electron microscope (SEM) analysis

SEM analysis is done to examine the morphological features and the state of dispersion of nano-fluorapatite in the polyurethane (PU) polymer. The micrographs showed that there is a very homogenized distribution of nanoparticles in low concentration (0.4 wt). When this loading, the nano-fluorapatite particles are evenly distributed in the polymer network, agglomeration or clustering could not be observed, which is a good sign of nanoparticles and polyurethane network compatibility.

Homogenous dispersion of nanoparticles is essential in the higher interfacial interactions between the polymer chain and the nanofillers, and this determines directly the mechanical and optical reinforcement of nanocomposites as well as the potential antibacterial activity of the nanocomposite. Spread nanoparticles do aid in the enhancement of the transfer of the load bearing element in the polymer structure, increasing the stiffness, strength and extending their longevity without affecting the natural flexibility and transparency of their polyurethane. The nanoparticle- matrix compatibility of the

PU/nano- fluorapatite composites is optimum at the observed concentration, which is critical in the application where the improved material performance of the material is required without compromising the inherent characteristics of the polymer. It means that the notable gains in functional properties can be obtained at low filler loadings without any negative outcomes like loss of opaqueness or brittle character.

Figure shows SEM images of pure polyurethane, and polyurethane mixed with 0.4 wt% nano-fluorapatite at different magnifications, which shows a homogeneous distribution of particles and the integrity of the microstructure of the composite.

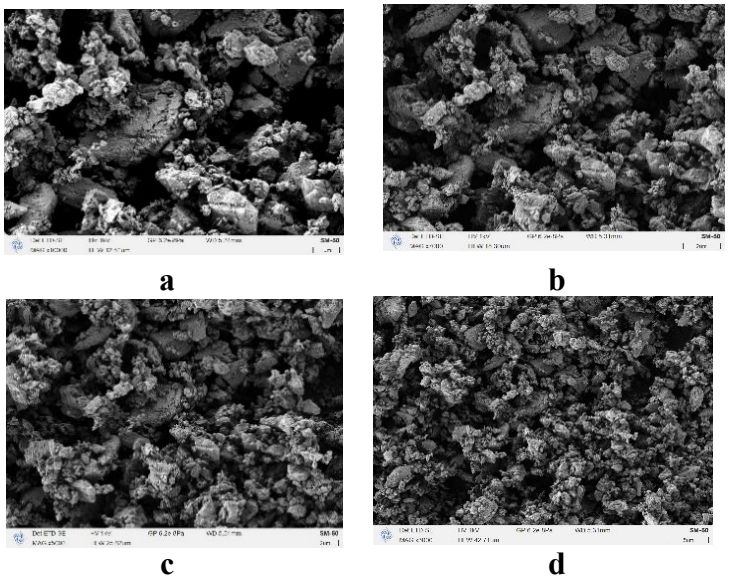

Figure 4 Morphology of polyurethane reinforced with 0.4 wt.% nano particles at various magnification.

3.2 Material strength characteristics
3.2.1 Micro-scale hardness test

Micro-scale hardness of pure transparent polyurethane (PU) that are usually used in dental aligners is determined to be 72 Shore D, and this value fits well within the general range of the flexible polyurethane materials deployed in orthodontics practice. Gradual increase in the Shore D hardness is observed after reinforcement of the PU matrix with nano-fluorapatite particle at different loadings. This tendency shows obviously that the restrained addition of nano- fluorapatite is effective in order to increase the hardness of the surface of the polymer composite. The enhancement in the hardness observed can be ascribed to the reinforcing effect of the nano- fluorapatite particles which enhance the load bearing capacity of the polymer matrix and limit the movement of polymer chains when subjected to a given stress. Also, the nanoparticles which are well dispersed create a microstructure which is less susceptible to deformation of the surfaces and results in substantial mechanical stability. It is remarkable that, nano- fluorapatite can give high levels of reinforcement at low concentrations (around 0.1 wt.% or a little more) without affecting the optical clarity of the substance, which is essential in dental aligners, as shown in Figure 5. Even though the percentage change between 72 and 85 Shore D may not seem significant numerically, it is a significant enhancement in mechanical performance and serviceability, especially in cases when cyclic loading and surface resistance are of importance. The increased hardness brings with it, increased resistance to abrasion and deformation of the surface during clinical use, which may increase the useful life of the aligners. There is the need to strike a balance between toughness and malleability. This hardness might be too high and therefore the material may not be able to fit in the anatomy of the teeth in a comfortable manner. The nano-

fluorapatite reinforcement developed in this work attained a good compromise whereby the hardness of the substance is enhanced without compromising the flexibility required in the effective and comfortable orthodontic extraction.

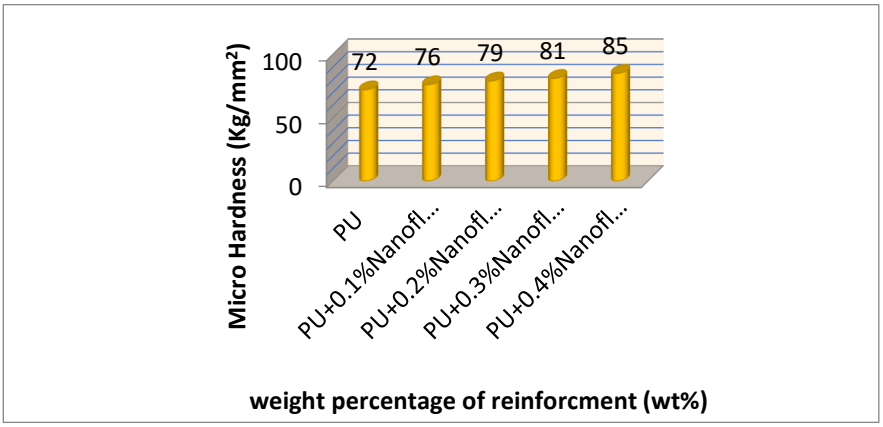

Figure 5 Hardness value of the pure polyurethane and various weight percentage of nano fluorapatite particle.

3.2.2 Tensile results

The base tensile strength of the pure transparent polyurethane (PU) which is used in dental aligners is 45 Mpa, and this is its inherent mechanical property of sustaining the stresses that it is likely to be exposed to in the normal usage of the orthodontics. This shows that the unreinforced PU matrix has enough structural integrity such that it is effective when subjected to working conditions of functional loading. Addition of nano-fluorapatite particles led to progressive increase in tensile strength of the PU matrix with addition of the nanoparticles at various loadings, up to 64, 71, 84 and 93 Mpa as shown in Figure 6 at increasing nanoparticles concentration. Such strength increase in tensile performance shows that nano-silica reinforces the polymer matrix. This increase in tensile strength is as a result of a number of factors. The physically dispersed nanoparticles affect the polymer chains by reducing their mobility and the chains cannot slip past each other as tensile stress is applied on them. As a result, the material will be able to resist greater loads. In the stretching process, some of the load is passed on to the nanoparticles and this is useful in reducing local stress concentration, slows down crack propagation and enhances a more homogenous distribution of stress in the entire composite. Nano-fluorapatite is present and this is successful in strengthening the polymer network, which improves the stiffness and tensile strength. Moreover, the nanoparticles enhance the enhancement of the modulus of elasticity by restricting the mobility of the polymer chains in the matrix, which makes the composite firmer, but at the same time, gives it enough flexibility [27]. This mechanism of stress transfer and restriction to a chain mobility all results in the creation of a more cohesive and stronger material that can perform better when subjected to strenuous orthodontics.

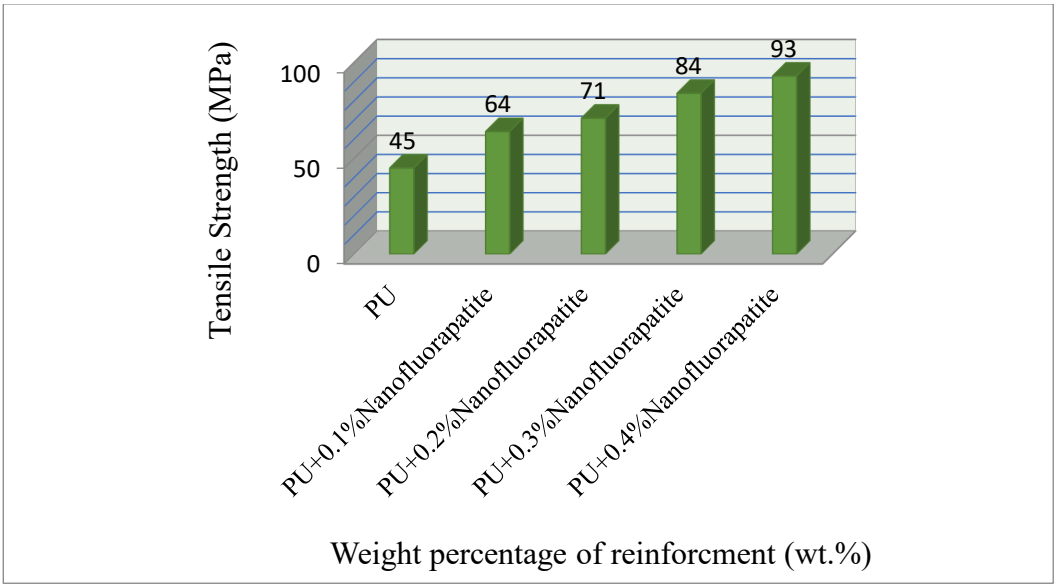

Figure 6 Tensile strength value of the pure polyurethane and various weight percentage of nano-fluorapatite particles.

3.3 Biological results

3.3.1 Antibacterial results

Bactericidal activities of the five polyurethane (PU) samples reinforced with different nano-flora (n-FAp) concentrations (0.1 0.4 wt.%) are observed to depend intensely on the surface activity of the reinforced nanoparticles as well as the quality of their dispersion. The addition of even low concentration of n-FAp resulted in a significant change of the surface morphology and surface chemistry of the PU matrix, thus leading to a low level of bacterial adhesion as opposed to the unreinforced polymer. With the increasing level of n-FAp content, the antibacterial efficiency progressively improved, which can be explained by the fact that the dispersion of fluorapatite nanoparticles is homogeneous, which also results in greater accessibility of nanoparticles to the surface of the material. Interestingly, the sample which had 0.4 wt.% n-FAp had a spectacular percentage inhibition of bacteria at 92 percent confirming that the concentration of the nanoparticles is predominant in inhibiting bacteria growth. It is linked to this improved antibacterial performance, which can be explained by the capacity of n-FAp to destabilize bacterial cell membranes, minimize microbial adhesion, and prevent biofilm formation due to the change of surface roughness and ionic interaction. Therefore, the antimicrobial performance of the composite material has been enhanced significantly because the effective dispersion of n-FAp nanoparticles effectively prevents the colonization of bacteria on the PU surface [28]. The detailed antibacterial results are presented in Figure 7.

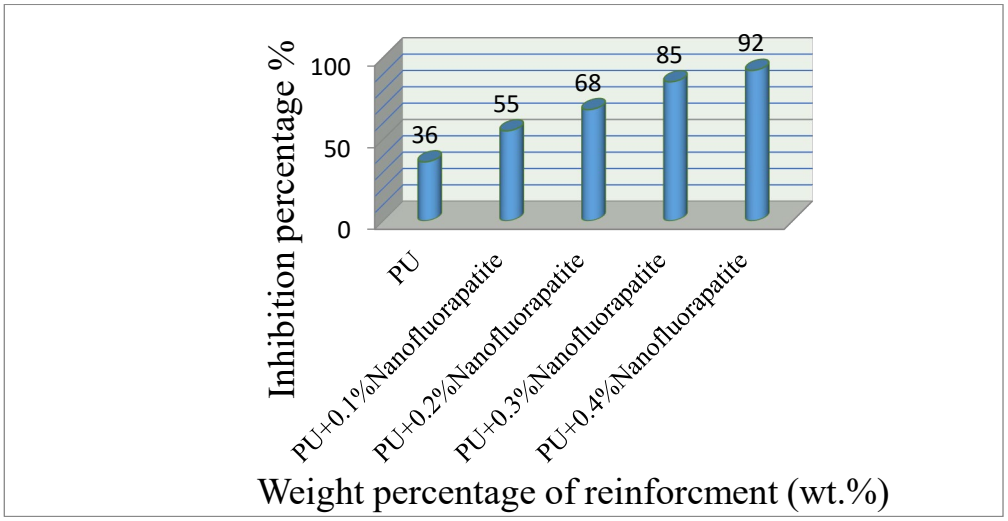

Figure 8 Antimicrobial results.

3.3.2 Cytotoxicity test by hemolytic assay results

As a quantitative measure to determine the blood compatibility of the tested materials, the rate of hemolysis is adopted (in percent), which is reflected on the spectrophotometric measurements of the released hemoglobin under an absorbance wavelength of 520 nm. The addition of nano-fluorapatite (n-FAp) into the polyurethane layer is an important factor that determines the relationship between the surface of the material and red blood cells. Its findings showed that PU/n-FAp composite samples all showed negligible levels of hemolysis as compared to the positive control (-C), which portrays the material to be highly hemocompatible and this proves that the materials are not toxic to human blood cells. This desirable character is credited to the bioceramic character of n-FAp that increases surface bioactivity, stabilizes cell membranes and minimizes the undesirable interactions between ionically opposing forces that otherwise may lead to rupture of the red blood cells. Moreover, the analysis of the cytotoxicity, which is provided in Figure 8, indicates that the biological response of the materials can also be limited not within the area of blood compatibility and can also be a specificity of interactions with cancer cells. The observation reinforces the potential anticancer effect of the n-FAp reinforced PU composites, but at the same time, it is safe to normal human cells. All in all, the findings support the notion that the use of n-FAp can greatly enhance the biocompatibility profile of PU without causing hemolytic responses, which makes it appropriate to use in biomedical practice [29,34].

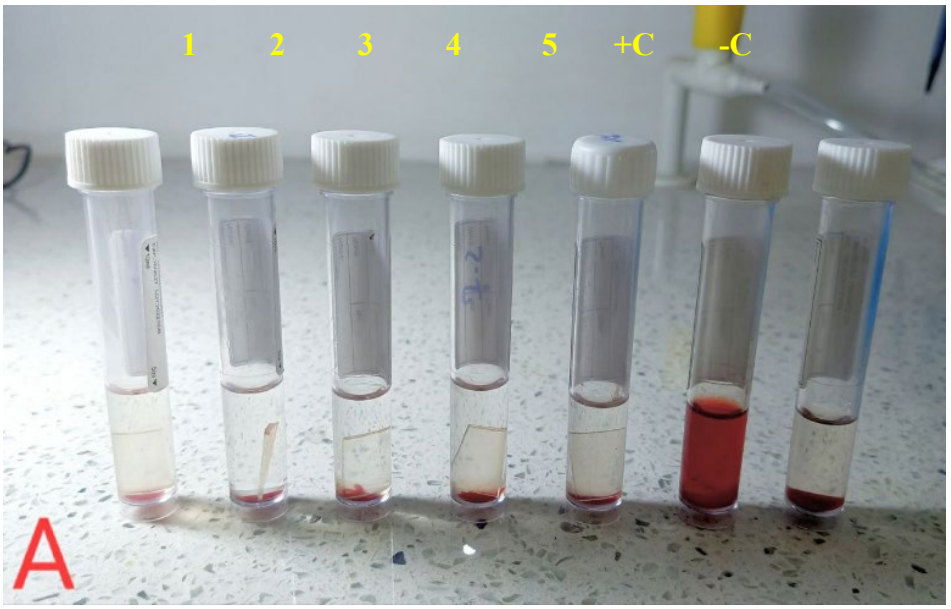

Figure 8 Results of the qualitative and morphological hemolysis test conducted within test tubes after incubation.

4. CONCLUSIONS

Based on the experimental tests and the obtained results, this study demonstrates the effectiveness of reinforcing polyurethane (PU) with nano-fluorapatite (n-FAp) to enhance its suitability for clear dental aligner applications. The following conclusions can be drawn:

1. Polyurethane (PU) was selected as the base material for clear aligners due to its flexibility, optical transparency, and biocompatibility. Fluorapatite nanoparticles with an average particle size of approximately 53.5 nm were incorporated into the PU matrix at four different weight fractions (0.1%, 0.2%, 0.3%, and 0.4%) to improve its mechanical and biological performance.
2. The FTIR analysis indicated effective introduction of nano-fluorapatite into the PU matrix that did not change the basic chemical form of the polymer. All the samples contained the characteristic absorption band of PU such as, -OH stretching (3300-3500 cm^{-1}), C-H stretching (2920-2950 cm^{-1}), carbonyl groups (C=O, 1700-1730 cm^{-1}) and N-H and C-N bands of PU (1530-1570 cm^{-1}). The formation of PO_4 -related bands and their progressive development in the areas of 11001000 cm^{-1} and 600560 cm^{-1} proved the existence of n-FAp and showed physical interactions, primarily, hydrogen bonding, between the polymer chains and the nanoparticles.
3. The analysis of SEM showed that n-FAp is homogeneous dispersed in the PU matrix, especially at low concentrations of nanoparticles, and no agglomeration effect was detected. This even distribution increases the number of interfacial bonds, efficacy of stress tabulation, and is a critical factor in optical clearness and structural strength.
4. The measurement of mechanical hardness indicated that pure PU was hard with a hardness of about 72 Shore D which proved its flexibility and ability to be used as a clear aligner. The increment in the hardness by the introduction of n-FAp was gradual, being increased to greater values by the reinforcing effect of the rigid nanoparticles, which inhibit the movement of polymer chains and increase the deformation resistance.
5. The tensile strength of pure PU (45 MPa) was also proven with tensile testing, where the tensile strength of 45 MPa was raised up to between 48 and 93 MPa with the addition of n-FAp. This can be explained by the fact that it is improved in load transfer, crack initiation and propagation, and the presence of a more stable and rigid microstructure due to the even dispersion of the nanoparticles.

6. The effect on the biological performance of the composites due to the incorporation of nano-fluorapatite was significant. The optimal dispersion of nanoparticles in the polymer matrix was essential in boosting the antibacterial activity without compromising on non-toxicity and high biocompatibility, thus render the developed PU/n-FAp composites to be safe to be used in biomedical and orthodontic practices.

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