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A study on tung oil-infused polyurea microcapsules: Prioritizing self-healing with bioassay-based toxicity and antibiofilm evaluations

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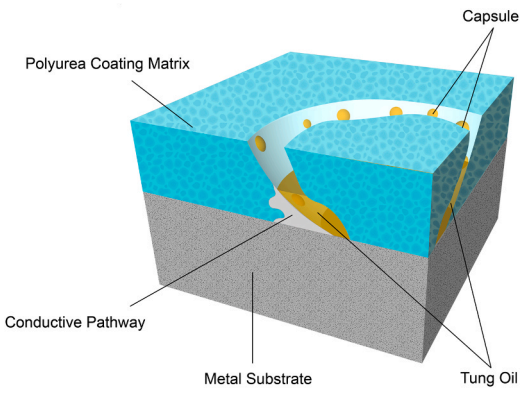
GRAPHICAL ABSTRACT



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ABSTRACT

This study presents a novel approach to enhancing the longevity and efficacy of dental materials through the incorporation of Tung oil into polyurea microcapsule coatings. Tung oil is renowned for its superior moisture barrier and antimicrobial properties, and when merged with the durable nature of polyurea, it creates a coating poised to substantially improve self-healing capabilities in dental applications. Focusing on the dual objectives of mechanical fortitude and biocompatibility, this research meticulously evaluates the coatings' proficiency in withstanding the rigors of the oral environment and their compatibility with oral tissues. Employing a suite of bioassays, we meticulously assess the toxicity and antibiofilm characteristics of these coatings, in addition to their self-healing efficiency. These evaluations measure the coatings' ability to autonomously repair physical damage and counteract microbial colonization. The results reveal that tung oil significantly enhances the polyurea matrix's intrinsic self-repair features, which proves crucial in resisting the abrasive and microbial challenges prevalent in the oral cavity. The modified coatings demonstrate marked improvements in wear resistance and microbial interaction, heralding a significant advancement in dental material technology. This in-depth

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analysis corroborates the amplified capabilities of Tung oil-infused polyurea coatings and paves the way for future investigations into the integration of natural oils within medical-grade material design, opening a new chapter in the synthesis of biomaterials tailored for oral healthcare advancements.

1. Introduction

The oral cavity, an environment fraught with mechanical, chemical, and biological challenges, imposes strenuous demands on dental materials. Sustained mechanical stresses from mastication, erosive chemical interactions from dietary acids [1], and continuous exposure to oral microorganisms are critical factors that precipitate the degradation of dental restoratives, thereby curtailing their functional lifespan [1,2]. Within this context, the advent of self-healing coatings has emerged as a strategic response to enhance the durability and integrity of dental applications. These novel materials are engineered to autonomously remediate micro-damages, potentially extending the serviceability of restorations while concurrently diminishing the frequency of dental interventions [3]. This evolution in material science promises significant improvements in patient care through increased restoration longevity, thereby contributing to a more cost-efficient dental healthcare system.

In the search for viable solutions, polyurea coatings have garnered attention as prospective assets in dental applications, attributed to their formidable mechanical fortitude, resistance to chemical insults, and latent self-healing faculties [3]. Their rapid polymerization responses engender a resilient matrix that offers substantial protective benefits to substructural elements. Despite these attributes, the adaptation of polyurea coatings for dental utility encounters formidable obstacles, notably biocompatibility [4,5], to ensure non-toxicity and oral tissue compatibility. Furthermore, the distinctive mechanical and moist conditions of the oral environment pose significant challenges to the operational efficacy of self-healing mechanisms, traditionally conceptualized for drier contexts [1,4]. Despite the auspicious attributes of polyurea, the translation of its use to dentistry necessitates rigorous scrutiny of its biocompatibility and toxicity—imperative considerations given the intimate contact with oral tissues. The oral cavity's unique amalgam of mechanical stressors and persistent moisture creates a challenging environment for the implementation of self-healing mechanisms [5], necessitating modifications to these materials for optimal function within such a wet setting.

Drying oils, esteemed for their eco-friendly corrosion resistance, have been integral to various applications [6] such as in paint formulations, waterproofing agents, and components in joint sealants and masonry mortar. Notable among such oils are Linseed oil and Tung oil, which are predominantly composed of triglycerides, featuring a rich content of polyunsaturated fatty acids like alpha-linolenic acid. The capacity of these triglycerides to undergo oxidative cross-linking, transforming into a durable film upon exposure to air, is attributed to the abundance of double bonds within their fatty acid chains [7–9]. As renewable resources sourced from plant seeds, drying oils represent a sustainable option in the production of protective films [2,3]. Specifically, Tung oil is distinguished by its conjugated double bonds, conferring upon it an accelerated drying capacity relative to the non-conjugated structure of Linseed oil. The cross-linking process in Tung oil commences with the formation of peroxide linkages which subsequently evolve into more stable ether cross-links, contributing to a more robust and enduring film [9].

In the domain of dental material science, the novel introduction of Tung oil-infused polyurea microcapsules marks a significant innovation tailored to meet the demanding conditions of the oral environment [10]. Tung oils, with a historical pedigree of use in protective finishes, offer a distinctive combination of properties including the formation of a robust and hydrophobic barrier [2,8]. This is particularly advantageous in the moist oral setting, where resistance to chemical agents and biofluids is crucial. When amalgamated with polyurea, Tung oils not only bolster the inherent self-healing attributes of the microcapsules, enabling seamless repair of minor damages but also potentially obstruct the penetration of pathogenic entities [11,12]. In contrast to conventional modifying agents, Tung oils are heralded for its natural origin and biocompatibility, presenting a reduced toxicity profile that is of utmost importance in materials that engage intimately with human tissues [6]. This aligns with the escalating pursuit of sustainable and biologically harmonious materials in healthcare. The introduction of these Tung oil-modified coatings could revolutionize dental restoration practices by enhancing the durability and functional longevity of dental prosthetics [13], thereby diminishing the incidence of clinical re-interventions and augmenting the quality of patient care. This investigation into the synergistic potential of Tung oils and polyurea within dental applications seeks not only to refine the mechanical endurance and self-reparative capacity of restoratives but also to rigorously evaluate their biocompatibility and toxicity. The implications of such advancements extend beyond the prolongation of restoration life; they embody a paradigm shift towards integrating sustainability and patient safety into the forefront of dental material development.

2. Integration of tung oils into polyurea coatings for dental applications

2.1. Benefits of tung oils

The inherent chemical structure of Tung oil enables the formation of higher oligomers under identical conditions compared to counterparts like non-conjugated ethyl linoleate [10]. This results in films with a markedly enhanced resistance to moisture and alkaline environments, likely owing to the increased formation of resilient ether bonds [4–6]. Consequently, Tung oil yields a coating that is not only harder but also exhibits superior durability and water resistance than that derived from Linseed oil, as demonstrated in the structural analysis. The intricate chemical structures of the unsaturated fatty acids present in both Linseed and Tung oils, along with the anticipated structure of Tung oil, are elucidated in the accompanying illustrations. In the comparative analysis of drying oils, the performance of Tung oil is notably superior due to its chemical composition and structural properties, as detailed in Table 1 and Fig. 1. The table outlines the percentage of various fatty acids present in drying oils, showing a significant presence of conjugated fatty acids in Tung oil, specifically α-Eleostearic acid, which is a cis, trans, trans-triply conjugated fatty acid constituting 80 % of its composition (Figure S1). This high proportion of conjugated fatty acids is rare and imparts exceptional drying properties to Tung oil. In contrast, Linseed oil predominantly contains Linolenic acid, a non-conjugated fatty acid, contributing to 52 % of its composition [12]. The saturated fatty acids, such as stearic and palmitic acids, are relatively low in both oils, but their lower presence in Tung oil, at only 5 %, further contributes to its more desirable drying characteristics [14]. Saturated fatty acids do not participate in the drying process as effectively as unsaturated fatty acids, making their lower percentage advantageous.

Fig. 1**(a)** elucidates the chemical structure of unsaturated fatty acids found in both Linseed and Tung oils, such as Oleic acid (18:1) (a monounsaturated omega-9 fatty acid common in various plant oils) and Linoleic acid (18:2) (a polyunsaturated omega-6 fatty acid prevalent in Linseed oil), and presents the unique structures of gamma-Linolenic acid (18:3) and Eleostearic acid. The latter is instrumental in the drying process due to its conjugated structure, which facilitates the formation of a cross-linked, impermeable film upon oxidation. This ability to form a dense, protective layer is visually represented in the figure,

demonstrating the complexity and arrangement of bonds that allow for such reactions. Fig. 1**(b)** hypothesizes the plausible structure of Tung oil, illustrating the alignment of conjugated double bonds, which contributes to Tung oil's enhanced drying properties and the resultant robust, protective film ideal for coating applications. The dense array of conjugated double bonds within Tung oil's structure is what enables the rapid formation of cross-links upon exposure to air, resulting in a film that is both hard and water-resistant.

The mechanistic processes underpinning Tung oil's transformation involve initial auto-oxidation of dienes to form hydroperoxides, which then interact with other unsaturated chains, culminating in cross-linking and resin hardening. Figures delineate the sequential biochemical reactions, highlighting the potential for covalent bonding between Tung oil and a matrix to bolster stability, particularly in aqueous conditions. This stabilization through covalent bonding enhances the material's self-healing efficiency, as opposed to relying on weaker intermolecular forces [11]. Figure S1 references the work of S. Ataei et al., illustrating a potential reaction between coconut oil-based alkyd resin and amine groups. Analogously, in the context of this report, Tung oil's acid groups could react with polyamines in the polyurea matrix to form stable C-N covalent bonds. Such reactions are pivotal in mitigating conductive pathway formation, thereby preserving the integrity and functionality of the material.

2.2. Polymerization of tung oils by oxidation

The polymerization of Tung oil via oxidation is an intricate catalytic process, accelerated by the presence of transition metals which act as facilitators for cross-link formation. This oxidative polymerization is a multi-step reaction involving the following stages: (a) The **initiation** process ($\bullet R\bullet + O_2 \rightarrow ROO\bullet$) begins with the generation of free radicals from the unsaturated fatty acids within the Tung oil [14]. These radicals engage with molecular oxygen, leading to the formation of peroxyl radicals, initiating the polymerization process. Oxygen's role in the self-healing mechanism of Tung oil, both as a waterproof and anti-corrosive agent, is pivotal, and the presence of dissolved oxygen (DO) is a key factor in underwater self-healing processes [13,15]. Tung oil's oxidative polymerization, critical for its self-repair, relies on the availability of oxygen, which can be found dissolved in water bodies alongside atmospheric oxygen [11–13]. Dissolved oxygen, the measure of free, non-compound oxygen present in water, enters aquatic systems either via direct diffusion from the atmosphere or as a byproduct of photosynthesis [16]. Natural aeration, induced by wind or running water, and artificial means, such as aeration devices, contribute to the DO levels in water. The content of dissolved oxygen is not constant, varying with the aquatic environment's conditions influenced [15,16] by resident organisms, salinity, temperature, and vegetation cover; (b) Propagation ($\bullet ROO\bullet + RH \rightarrow ROOH + R\bullet$) process produces hydroperoxides and propels a chain of radical-driven reactions.The peroxyl radicals, noted for their reactivity, can then abstract hydrogen atoms from neighboring unsaturated fatty acid molecules; (c) Decomposition ($-ROOH +$ Transition Metal (e.g., Co^{2+}) $\rightarrow RO\bullet +$ Transition Metal (e.g., Co^{3+}) $+ OH^{-}$) leads by those hydroperoxides, which particularly in the vicinity of transition metal catalysts, undergo decomposition to produce alkoxy radicals and hydroxide ions. These species are subsequently involved in additional polymerization reactions, perpetuating the process; (d) Termination (Cross-linking) ($ROO\bullet + C{=}C \rightarrow RO{-}O{-}C{-}C\bullet$) process which is caused by the peroxyl radicals engaging with carbon-carbon double bonds in different fatty acid molecules, culminating in the creation of a cross-linked, stable polymeric matrix. This cross-linking is a cornerstone of the Tung oils' self-healing attributes, as it facilitates the material's ability to autonomously repair itself [17]. These coordinated chemical events are central to enhancing the self-healing functionality of Tung oil-infused polyurea, contributing to a resilient composite with the capacity for self-restoration [15,18]. The implication of such a polymerization process is particularly significant in dental restorative materials, where longevity and durability are of paramount importance. Through these mechanisms, a polymeric network is established that not only resists wear but can also effectively recover from damage, thereby potentially increasing the service life of dental restorations and reducing the frequency of dental interventions [18,19].

2.3. Incorporating poly urea-formaldehyde (PUF) microcapsules

Incorporation of Polyurea-formaldehyde (PUF) microcapsules into a matrix serves as a method to sequester a healing agent, preventing premature interaction with the matrix environment [3,5,10]. The encapsulation of the core material provides several advantages: it enhances the longevity of active agents, bolsters resistance to environmental factors, facilitates the handling of otherwise liquid substances by solidifying the core, and ensures the non-toxicity of any degradation products. The implementation of Polyurea-formaldehyde (PUF) microcapsules within dental materials also offers an innovative approach to enhance oral applications' durability and therapeutic efficacy [6,11]. The strategic encapsulation of a healing agent within these microcapsules serves not only to isolate it from premature interaction with the surrounding matrix but also to provide sustained release [20], a crucial feature for long-term treatment success. These microcapsules must demonstrate impeccable biocompatibility, as they are intended for use in the sensitive and complex oral environment.

The adhesion strength of coatings containing varying concentrations of PUF microcapsules was assessed using a pull-off adhesion test. The studies conducted by S. Ataei et al. observed that samples with a higher concentration of microcapsules exhibited a reduction in adhesion strength [19,21]. This reduction in adhesion may be attributable to the physical disruption of the coating matrix by the microcapsules. However, the integration of microcapsules did not substantially differ in mean adhesion strength from the control samples, indicating that the presence of microcapsules does not critically undermine the structural integrity of the coating [21]. Furthermore, the microencapsulated drying oil displayed notable self-healing and anti-corrosive properties [5,9] . The choice of material for the microcapsule's shell is pivotal to the functionality of self-healing systems. The shell must be compatible with both polyurea and Tung oil, chemically inert, and simultaneously possess the resilience and pliability to rupture under stress but remain intact otherwise[17,19]. In an oral application context, the microcapsules' shell materials are paramount and must meet rigorous standards

Table 1
Comparative analysis of fatty acid composition and properties in Linseed and Tung oils.

Oil Type	Saturated Fatty Acids (%)	Oleic Acid (18:1) (%)	Linoleic Acid (18:2) (%)	Linolenic Acid (18:3) (%)	Conjugated Fatty Acids (%)	Drying Time	Film Hardness	Water Resistance	Chemical Resistance
Linseed oil	10 (Stearic, Palmitic)	22	16	52	-	Slower	Less Hard	Moderate	Moderate
Tung oil	5 (Stearic, Palmitic)	8	4	3	80 (α-Eleostearic acid)	Faster	Harder	High	High

Note: Saturated fatty acids include stearic (18:0) and palmitic (16:0). The conjugated fatty acid in Tung oil is α-Eleostearic acid with a cis, trans, trans configuration contributing to its rapid drying and durable film formation.

[3–5,11]. They should exhibit compatibility with the oral milieu, maintain chemical stability against saliva and dietary acids, and possess the mechanical strength to withstand masticatory forces [18]. Importantly, they should exhibit a controlled response to damage—rupturing to release healing agents upon impact but otherwise maintaining their integrity [22]. The selection of PUF, and by extension Melamine-urea-formaldehyde (MUF), is grounded in these materials' strong mechanical properties and established record of biocompatibility [15,16,22]. Moreover, the surface characteristics of PUF microcapsules, which promote robust mechanical bonding with the dental matrix, are crucial for ensuring the longevity of dental restorations. MUF shells, leveraging the strength and heat resistance of Melamine formaldehyde (MF), present a bio-friendly option that aligns well with urea-formaldehyde (UF) systems to minimize potential formaldehyde release—a significant concern in medical applications due to the toxicological implications of formaldehyde [23]. Besides, such encapsulation technology may stand to revolutionize dental therapeutics by offering a means for in-situ restoration and protection of dental tissues, effectively acting as a reservoir of therapeutic agents that respond to the biological demands of the oral environment [12,13]. When these microcapsules are integrated into the dental materials, their interaction with the natural biological processes, such as saliva's buffering capacity and the constant flux of nutrients and waste, becomes a focal point of biocompatibility assessment.

2.4. Advanced microencapsulation techniques for tung oils in polyurea dental applications

The oral cavity is a complex environment where materials are exposed to various mechanical and biochemical challenges [13]. Tung oil's biocompatibility is a significant advantage here. Derived from natural sources, it is inherently less reactive and more harmonious with the biological tissues found in the oral cavity. Unlike synthetic materials, which can degrade into potentially toxic compounds [16], Tung oil is less likely to release VOCs or other harmful substances that could lead to inflammation, allergic reactions, or toxicity. This natural oil is metabolized by the body more readily, reducing the likelihood of negative long-term effects. Moreover, the oxidative polymerization of Tung oil does not rely on harmful catalysts or by-products that could leach out and compromise oral health. Instead, it forms a biologically inert network upon curing, which is less likely to provoke a biological response [18]. The development of advanced microencapsulation techniques for incorporating Tung oils into polyurea matrices marks a pivotal evolution in dental material science, with particular emphasis on self-healing applications. Traditional research on self-healing coatings has focused largely on atmospheric conditions, with less consideration given to performance in aqueous environments—a gap that becomes particularly relevant for dental applications exposed to the moist oral cavity [19]. Recent innovations have leveraged extrinsic mechanisms, using microcapsules to encapsulate Tung oil, ensuring its stability and uniform dispersion within the polyurea matrix [20,21]. This strategy effectively isolates the Tung oil, preserving its reactive potential by preventing premature interactions with the matrix constituents or the surrounding aqueous environment. By maintaining the integrity of the healing agent until needed, the microencapsulation approach significantly extends the service life of coatings.

The current research thrust aims to synthesize a coating system that demonstrates self-healing capabilities both in ambient air and submerged conditions. The research utilizes a melamine-urea-formaldehyde shell to encapsulate Tung oil, capitalizing on the microcapsules'-controlled release properties to activate the self-healing process upon exposure to water with adequate dissolved oxygen levels [21,23]. This encapsulation method not only focuses on the physical restoration of the material but also considers the implications of bioassay-based toxicity and antibiofilm evaluations. In dental applications, where the interaction with human tissues is inevitable, the biocompatibility of the material is paramount. The efficacy of the Tung oil-polyurea matrix in preventing biofilm formation, coupled with its low toxicity profile, will be rigorously tested, ensuring its suitability for long-term oral health applications.

3. Methodology

3.1. Materials

Materials selected for their exceptional purity from established suppliers, indicated as follows in Table 2, are critical for the fabrication of microcapsules and the resulting polyurea resin.

Table 2
Materials for polyurea and polyurea with integration of microcapsules synthesis.

Chemical	Purity	Supplier	Location
Melamine 99 108–78–1	99 %	Sigma-Aldrich	St. Louis, MO, USA
Urea 57–13–6	98 %	Fisher Scientific	Hampton, NH, USA
Formaldehyde 818708	37 wt% solution	Merck	Kenilworth, NJ, USA
Lauryl Sulfate Sodium (LSS)	99 %	Acros Organics	Geel, Belgium
Polyvinyl Alcohol (PVA) 088–60	98–99 %	Alfa Aesar	Haverhill, MA, USA
Tung Oil	100 % refined	Xuzhou Huide New Material Technology Co., Ltd.	Xuzhou, China
Methylene Diphenyl Diisocyanate (MDI)	98 %	Dow Chemicals	Midland, MI, USA
p-Phenylenediamine (p-PDA)	>99 %	BASF	Ludwigshafen, Germany
Tetrahydrofuran (THF)	>99.9 %	VWR Chemicals	Radnor, PA, USA
Polypropylene Glycol	95 %	Huntsman Corporation	The Woodlands, TX, USA

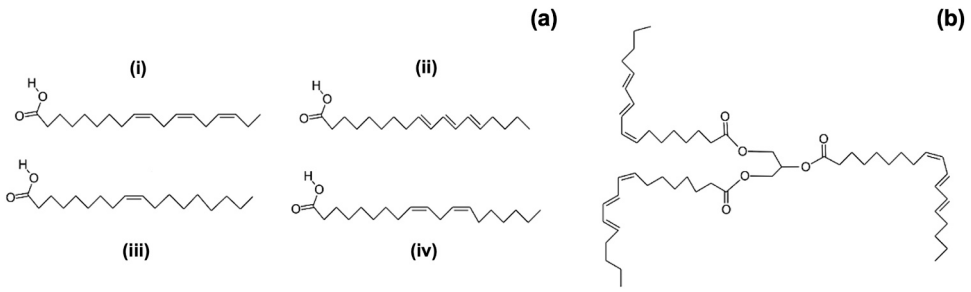

Fig. 1. Comparative chemical structures of fatty acids in drying oils (a) Chemical structures representative of fatty acids in Linseed and Tung oils: (i) Gamma-Linolenic Acid (18:3) – Found in plant oils; (ii) Eleostearic Acid – Tung oil's rapid-drying agent; (iii) Oleic Acid (18:1) – A monounsaturated fat; (iv) Linoleic Acid (18:2) – Common in Linseed oil and (b) Hypothetical structure of Tung oil.

3.1.1. Synthesis of melamine-urea-formaldehyde (MUF) microcapsules

Melamine-Urea-Formaldehyde (MUF) microcapsules were crafted using a refined in situ polymerization method within an emulsified medium. This process, based on a modified version of the technique established by J. K. Lee et al., was executed with a meticulously determined molar ratio of melamine (M), urea (U), and formaldehyde (F) at 3:1:8.5. The synthesis commenced with the preparation of aqueous solutions of Lauryl sulfate sodium (LSS) and Polyvinyl alcohol (PVA), with the former heated to 70 °C for 20 min and the latter kept at the same temperature for a more extended period of two hours. In a separate vessel, melamine and formaldehyde were reacted in distilled water at a controlled temperature of 25 °C to form a melamine-formaldehyde (MF) prepolymer over 25 min. Parallelly, urea was dissolved in water and subjected to agitation before its integration with the MF prepolymer. The addition of LSS and PVA to this mixture provided stability to the emulsion, which was then augmented by the gradual introduction of Tung oil. The resulting concoction was subjected to a sustained temperature of 86 °C and stirred continuously for five hours, fostering the formation of microcapsules. Upon completion of the reaction, the microcapsules were isolated, filtered, and left to dry at room temperature, yielding a product ready for integration into the polyurea dental matrix.

3.1.2. Synthesis of polyurea and integration of microcapsules

In the synthesis of the polyurea matrix for integration with microcapsules, two primary reactants are involved [8,11]. Methylenediphenyl diisocyanate (MDI), forming Part A of the mixture, is dissolved in Tetrahydrofuran (THF). Concurrently, Part B is created by dissolving p-Phenylenediamine (p-PDA) in THF, which is then stirred continuously for one hour to ensure complete dissolution. These two parts, MDI and p-PDA solutions, are then meticulously combined, adding a reactive diluent into the mixture at a precise 3:1 ratio to ensure optimal reactivity. Following the preparation of the polyurea matrix, Melamine-Urea-Formaldehyde (MUF) microcapsules, containing the healing agent Tung oil, are homogeneously incorporated into the resin. This dispersion is achieved through mechanical mixing at 200 revolutions per minute (rpm) for a duration of five minutes, ensuring an even distribution of microcapsules within the matrix. Once mixed, the composite material is applied onto a prepared steel panel with the use of a film applicator, spreading it evenly to achieve a consistent coating. The coated panel is then left to cure under ambient room conditions for a period of seven days to achieve full polymerization and hardening of the polyurea matrix. The chemicals involved in this procedure are selected based on their weight percentages to create the optimal balance between the MDI and p-PDA components. The detailed composition of Part A includes a range of 65.0–70.0 % MDI, with specific forms of the compound, such as the homopolymer, accounting for 28.0–33.0 % and additives like triethyl phosphate being present at no more than 2.0 %. Part B, primarily consisting of p-PDA at up to 100 %, also includes polyoxypropylenediamine and O-(2-Aminopropyl)-O′-(2-methoxyethyl) polypropylene glycol, ensuring the reaction readiness and processability of the polyurea. Tetrahydrofuran, with a purity of over 95 %, is used as a solvent to facilitate the dissolution and reaction of these components.

3.2. Characterizations

3.2.1. Fourier transform infrared (FTIR) spectroscopy

For FTIR spectroscopy, the coating samples were finely ground with potassium bromide, pressed into pellets, and analyzed using a Frontier PerkinElmer spectrometer with an ATR attachment [8,21]. This was done following ASTM E1252 to identify the functional groups in the Tung oil and polyurea matrix. Spectroscopic scanning was performed over the mid-IR range to elucidate the distinct functional groups within the Tung oil and polyurea matrix [24].

3.2.2. Self-healing evaluations

- ***Scratch Test:*** The coated steel plates were submerged in ambient water (25°C) to simulate the wet conditions of the oral cavity. Following immersion, each plate underwent a standardized scratch test per ASTM D7027 using an instrumented scratch machine [12–14]. This test applied a controlled force mimicking the scratching from masticatory activities. A control sample with 10 wt% tung oil and experimental samples with varying Tung oil concentrations (2 wt% to 10 wt%) were prepared to evaluate the self-healing efficacy. Over one week, the healing process was monitored, focusing on scratch closure and surface restoration to assess the effectiveness of Tung oil release and determine the optimal concentration for self-healing properties.
- ***Scanning Electron Microscopy (SEM) Analysis of Self-Healing:*** To examine the self-healing mechanism at the microstructural level, polyurea microcapsules (PUA-MCs) infused with tung oil were carefully sectioned and prepared for Scanning Electron Microscopy (SEM) [23]. The samples were affixed onto SEM stubs using conductive adhesive tape to ensure stability during electron imaging. To enhance electron conductivity and image clarity, the samples were sputter-coated with a thin layer of gold. Imaging was performed using a JEOL 6360LV SEM, with magnifications ranging from 50x to 100,000x. This process allowed for detailed observation of the microstructural changes and the efficacy of Tung oil release from the microcapsules during the healing process, adhering to the standards set by ASTM E1508.
- ***Tensile Strength Test:*** To assess the mechanical integrity post-healing, an adhesion test was performed as per ASTM D3359, which measures the adhesion of coatings by applying and removing tape under standardized conditions [25]. An MTS Criterion Model 42 Static Mechanical Tester, equipped with appropriate load cells, was used to apply a uniform force to the samples before and after healing, ensuring the reliability of the self-healing process.

3.2.3. Bioassay-based toxicity and antibiofilm evaluations

- ***Antimicrobial Evaluations:*** *Streptococcus mutans*, a primary contributor to dental biofilms, is cultured in a nutrient-rich medium optimized for oral bacteria, maintaining conditions that mimic the oral cavity's temperature and pH. A CDC biofilm reactor is employed to grow biofilms on coated samples, under conditions that replicate the oral environment with a constant temperature of 37 °C, analogous to human body temperature [16,21,23]. The inoculated reactor operates at a rotation speed conducive to biofilm formation, with samples exposed to a combination of ambient light and periodic UV irradiation to simulate the intermittent exposure to light in the oral cavity. The experiment includes a temperature gradient (from 25 ℃ to 35 ℃) to understand the biofilm resistance at various temperatures within the human mouth, especially considering the consumption of foods at different temperatures. Biofilms are stained using the FilmTracer LIVE/DEAD Biofilm Viability Kit to differentiate between live and dead cells. The Carl Zeiss LSM 780 laser scanning confocal microscope visualizes biofilm integrity and depth on the polyurea.
- ***Cytotoxicity Evaluation (MTT Assay for Cell Viability):*** The MTT assay, a standard colorimetric technique, evaluates cell viability by measuring the conversion of the water-soluble MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) reagent into an insoluble blue-violet formazan by metabolically active cells [19,20]. This procedure adheres to the guidelines set forth in ISO 10993–5. For the assay, L929 cells were plated at a density of 100,000 cells/mL in 96-well plates and cultured for 24 h to achieve semi-confluency under 37.0 ℃. After 24 hours of incubation, the sample solutions were removed, and the cells were treated with 50 μL of MTT solution (1 mg/mL in PBS). Following the incubation, the MTT solution was

discarded, and 100 μL of isopropanol was added to dissolve the formazan crystals fully. The resulting solution's absorbance was measured at 570 nm using an ELISA plate reader. This test was performed in triplicate to ensure reliability and reproducibility. Cytotoxicity was determined by exposing cells to 100 % extraction of the test materials, specifically PUA-p-PDA and PUA-MCs, along with controls. After 24 h, the cells were stained using calcein AM for live cells and ethidium homodimer-1 for dead cells, facilitating differentiation under a confocal laser microscope. The staining resulted in live cells emitting green fluorescence, while dead cells exhibited bright red fluorescence. The proportions of live and dead cells were quantitatively analyzed using ImageJ software, based on the normalized surface areas of the respective fluorescence intensities.

Statistical evaluations for both bioassay-based toxicity and anti-biofilm evaluations were conducted using one-way ANOVA and the independent t-test (without assuming equal variances); results yielding a p-value ≤ 0.05 were deemed statistically significant. All statistical computations were carried out using SPSS PASW version 21.0 (SPSS Inc., Chicago, IL, USA).

4. Results and discussion

4.1. FTIR analysis of tung oils, MUF microcapsules and polyurea coatings

The Fourier-Transform Infrared (FTIR) spectroscopic evaluation of Tung oil unveils its molecular architecture, presenting prominent peaks within the infrared region (Fig. 2). The absorption bands at approximately 2933 cm^{-1} and 2924 cm^{-1} align with the C-H stretching vibrations commonly associated with aliphatic chains. The distinct peak appearing near 1751 cm^{-1} is representative of the C═O stretching vibrations, a hallmark of the ester functionalities presents in the fatty acid derivatives comprising the oil. Additionally, the absorption at about 1654 cm^{-1} is attributed to the C═C symmetric stretching, signaling the unsaturated character of the oil. Bending vibrations of C-H are discernible at approximately 1456 cm^{-1}, consistent with the presence of methylene (-CH_2-) and methyl (-CH_3) groups. Conversely, the FTIR spectrum for MUF microcapsules exhibits a discernible peak at 2924 cm^{-1}, analogous to that observed in Tung oil's spectrum. This

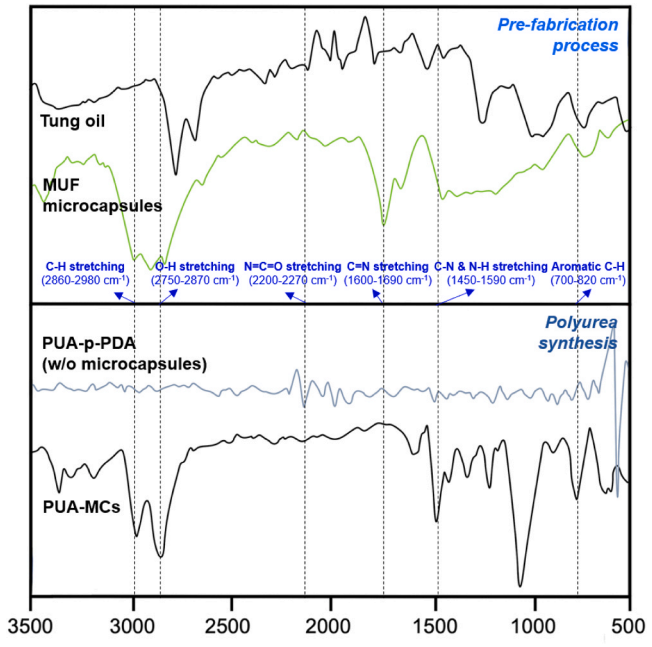

Fig. 2. FTIR spectrum of Tung oil, MUF microcapsules, PUA-p-PDA (without microcapsules), and PUA-MCs.

spectral concordance suggests the preservation of Tung oil's intrinsic chemical identity following its encapsulation within the MUF framework, thereby substantiating the successful integration of the oil into the microcapsules.

The FTIR spectrum for the polyurea-p-phenylenediamine (PUA-p-PDA) constructs showcases a multifaceted array of peaks, signaling the presence of diverse chemical bonds and hinting at potential residual reagents or complex formations, as denoted by the absence of specific urea linkage peaks [22]. The band identified between 2275 and 2250 cm^{-1}, indicative of the N═C═O isocyanate group, points to the existence of unreacted MDI constituents. This peak is pivotal as it indicates the presence of unaltered MDI within the composite. Absorption bands between 3500 and 3300 cm^{-1} and between 1630 and 1600 cm^{-1} are ascribed to the N-H stretching and C-N-H bending vibrations, respectively, suggesting the incorporation of p-PDA's primary amine functionalities in the formation of urea linkages. When juxtaposing the FTIR spectra of PUA-MCs against PUA-p-PDA, the parallelism in peak profiles, particularly those coinciding with the standalone microcapsules, authenticates the encapsulation of Tung oil within the polyurea matrix. This spectral similarity infers the successful entrapment of Tung oil and intimates that the polyurea framework may serve as an effective medium for promoting self-healing properties through the embedded Tung oil-enriched MUF microcapsules.

The FTIR spectral analysis lays a robust groundwork for delineating the chemical interactions and structural components of Tung oil and MUF microcapsules. The spectral continuity between the raw Tung oil and its encapsulated form within the MUF microcapsules substantiates the encapsulation efficacy. The spectral comparison between the PUA-p-PDA and PUA-MC systems validates the incorporation of Tung oil into the polyurea matrix, accentuating the prospects for devising self-healing materials. However, the detection of residual MDI via FTIR spectroscopy raises concerns regarding the reaction's thoroughness and the consequent material attributes. Full conversion of reactants is imperative not just for optimal material functionality but also for safety considerations, as MDI is a known sensitizing agent [18,21]. Hence, the cytotoxicity testing via MTT assay, which can measure cell metabolic activity as an indicator of cytotoxicity was deployed in the following section. And such method is also commonly used to assess the effect of materials on cell viability.

4.2. Self-healing evaluation

4.2.1. Scratch test analysis of self-healing

Fig. 3 provides a visual sequence of the self-healing process of polyurea acrylate (PUA) when integrated with microcapsules. The series begins with Fig. 3**(a)**, which shows the application of a manual force via a penknife to separate the cured material, simulating damage. Progressing to Fig. 3**(b)**, we witness a rapid initial healing phase where the manually separated parts display a strong adhesive quality upon contact; the two pieces bond together almost instantaneously, suggesting an active self-healing mechanism at work. This quick bonding is an indication that the microcapsules are releasing their contents and facilitating the healing process [22]. Fig. 3**(c)** illustrates the culmination of the self-healing process, where the material, after a certain time period, appears to be intact and shows no visible signs of the initial separation, evidencing a completed healing effect. This self-healing capability of PUA-MCs can be substantially attributed to the core-shell structure of the microcapsules which contains a healing agent that is released upon damage. The prompt and efficient recovery of material integrity showcases the potential for this technology in applications where material durability and self-repair are critical. The imperfections observed in the control sample without microcapsules, such as air bubbles and cracks, highlight the role of microcapsules in the healing process. These imperfections result from the material's intrinsic characteristics influenced by the use of methylene diphenyl diisocyanate (MDI) and the absence of a healing agent to repair the damage actively. The transition from

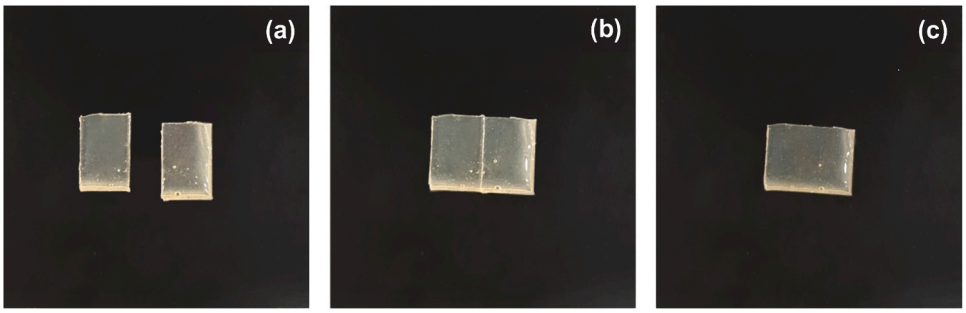

Fig. 3. The process of self-healing for polyurea coating with microcapsules (PUA-MCs) (a) manual separation by penknife, (b) demonstrating a significant initial healing effect, and (c) completed healing effect.

tetrahydrofuran (THF) to water as a solvent for the PUA-MCs is crucial, given the solvent's role in dissolving the healing agent p-phenylenediamine (p-PDA). THF's lower boiling point makes it less suitable for dissolving p-PDA, which has higher solubility at elevated temperatures, and thus, water is the preferred solvent. Despite the better solubility dynamics with water, its volatility at room temperature and the tendency of p-PDA to oxidize upon air exposure are challenges that need to be managed to ensure the integrity and efficacy of the self-healing system.

4.2.2. Scanning electron microscopy analysis of self-healing

The SEM image in Fig. 4**(a)** displays the self-healed polyurea control sample containing microcapsules (PUA-MCs). A noticeable gap at the interface of the two joined pieces reflects an incomplete healing process, with the failure to achieve a perfectly smooth surface. This gap, primarily attributed to the manual cutting with a penknife, signifies that the uneven surfaces could be limiting the effectiveness of the self-healing mechanism. Such irregularities could be mitigated by employing a more precise cutting tool, such as a universal cutter, which could provide a cleaner incision and potentially allow for better contact and healing. Previous reports indicate that these gaps can be filled by the healing agent released from the microcapsules, suggesting that while the healing is not visually perfect, on a microscopic level, the healing agent is likely performing its intended function of bridging the cut areas. Whereas the Fig. 4**(b)** showcase the clustered nature of the microcapsules. The aggregation of these microcapsules could be indicative of suboptimal fabrication or post-synthesis treatment methods. This clustering could impede the dispersion of the microcapsules within the coating matrix, which is essential for effective self-healing. The use of vacuum drying, as opposed to air drying, is suggested as a superior method for drying the microcapsules, as it reduces moisture content more effectively, potentially preventing the microcapsules from sticking together. Vacuum drying involves using a vacuum pump in an airtight chamber, which allows for a lower pressure environment where moisture can be removed more efficiently from the microcapsule surfaces [26]. This method might lead to better-dispersed microcapsules that could then be uniformly distributed in the coating matrix, optimizing the self-healing functionality. This rough morphology is conducive to good mechanical interlocking with the polyurea matrix, which is critical for the structural integrity and performance of the coating. The spherical shape is ideal for encapsulation as it can maximize the volume of healing agent stored and ensure that the agent is readily available for release upon the occurrence of damage.

4.2.3. Tensile behavior assessment of polyurea coatings

The tensile behavior of PUA-MCs was characterized by a non-linear load-extension relationship, displaying distinct peaks at certain extension intervals before the self-healing phase. These peaks may suggest multiple yielding points, which could be indicative of the coating's complex structural response to stress. The maximum force endured by the material before failure was recorded at 276.7 N. This performance demonstrates a degree of ductility, with the coating exhibiting further elongation under stress rather than immediate rupture [27]. The initial reduction in load capacity was attributed to slippage at the gripping interface, despite modifications made to improve grip, such as the incorporation of abrasive surfaces. Post-self-healing, the material was re-examined to ascertain the recovery of tensile strength, which was found to be 49.6 N (Fig. 5).

This represents an estimated 18 % restoration of the initial mechanical strength. This relatively modest recovery may be attributed to the healing process proceeding without external accelerants, such as heat or ultraviolet light, which are often pivotal in facilitating the necessary chemical reactions for self-healing in polyurea systems. The experimental findings showcase the intrinsic material properties of PUA-MCs, which include the ability to withstand substantial deformation prior to the grip failure, reflecting a material quality that is beneficial for applications necessitating high elasticity and energy absorption. Nonetheless, the reduced efficiency in self-healing underscores the necessity for an optimized healing protocol, potentially incorporating external stimuli to aid in achieving a more complete restoration of mechanical

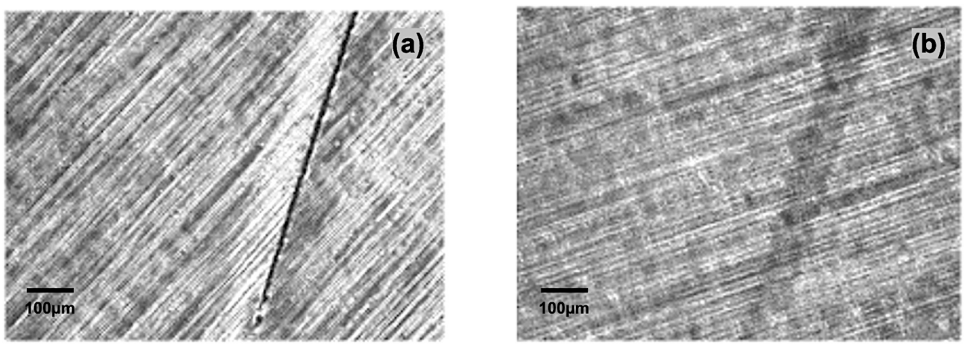

Fig. 4. SEM image of (a) The self-healed polyurea control sample with microcapsules (PUA-MCs) and SEM image (b) microcapsules clustered together.

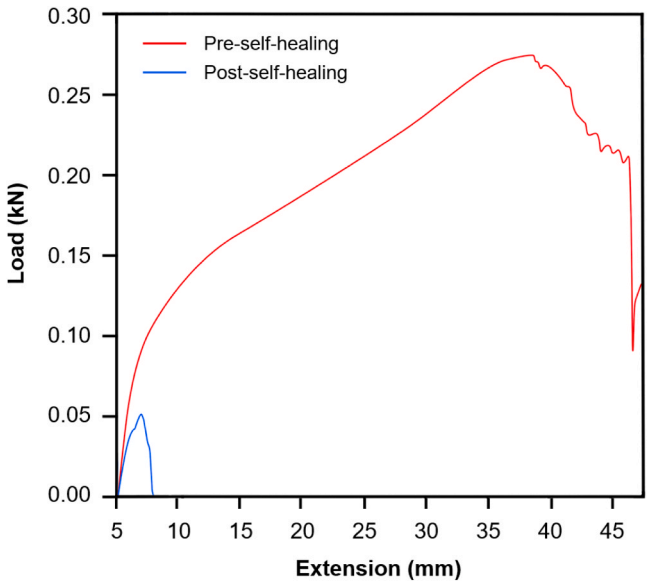

Fig. 5. Tensile behavior of pre- and post-self-healing PUA-MC coating samples.

properties. Considering the oral environment application, the feasibility of employing such self-healing polyurea coatings hinges on several factors. The oral cavity presents a challenging milieu due to its constant exposure to mechanical forces from mastication, temperature fluctuations from food intake, and a chemically active environment owing to saliva and various ingested substances. The modest recovery rate of the material's mechanical properties suggests that while it has potential, the current self-healing mechanism requires enhancement to ensure reliability within such a dynamic setting [28].

4.3. Cytotoxicity testing via MTT assays

The cytotoxicity evaluation of polyurea coatings integrating both qualitative observations and quantitative measurements, provides a robust framework for understanding the biological impacts of novel dental materials. It emphasizes the importance of continued research and development in dental material sciences to enhance therapeutic outcomes and patient satisfaction.To further enhance the study's accuracy, live and dead cells were distinctly stained using calcein AM and ethidium homodimer-1, respectively, facilitating their differentiation under a confocal laser microscope [18,27]. The proportions of live and dead cells were quantified with ImageJ software, offering a detailed view of the cytotoxic effects of the tested materials over time. The experimental results in Fig. 6 revealed distinct behaviors between the two coatings. PUA-MCs demonstrated a slight, though not statistically significant, increase in cell viability, from 74.49 % on Day 1–76.02 % on Day 7 (Table S1). The variability within these results, indicated by standard deviations and errors, suggests that while the coating maintains cell viability, its influence on cell proliferation is not pronounced. The lack of statistical significance in these changes, evidenced by p-values exceeding 0.95, implies that any observed improvements in cell viability could be due to natural variability rather than an intrinsic property of the coating. In contrast, the PUA-p-PDA coating exhibited more significant improvements in cell viability, particularly noted between Day 3 and Day 7, where it increased from 60.72 % to 62.50 %. This change, unlike the trends observed with PUA-MCs, was statistically significant with a negative p-value ≤ -2.24, highlighting a potentially beneficial effect of the PUA-p-PDA coating in supporting cellular health over time. These findings are particularly relevant in the context of dental applications, where materials must exhibit sustained biocompatibility to prevent adverse reactions and support tissue integration. The suitability of PUA-p-PDA for dental applications can be attributed to its better performance in maintaining cell viability, which suggests its potential to reduce inflammatory responses and enhance the longevity of dental implants and coatings. Dental materials require not only mechanical strength but also biocompatibility to ensure they do not invoke cytotoxic reactions or hinder the natural functions of cellular components within oral tissues.

Tung oil, known for its protective finishes in various applications, does have its concerns regarding toxicity when ingested or improperly handled, as it can cause symptoms like nausea, stomachache, headache, and skin irritation [28]. However, its use in materials such as PUA-MCs for dental applications warrants careful consideration, especially given the controlled environment in which these materials are synthesized and applied. The cytotoxicity assays, particularly the MTT assay results for PUA-MCs, are crucial in understanding why such a material might still be considered for dental uses despite the potential toxicity of one of its components, like tung oil. From the data provided and discussed previously, PUA-MCs demonstrated a slight increase in cell viability over time from 74.49 % on Day 1–76.02 % on Day 7. These results, though showing only a marginal improvement, did not display significant cytotoxic effects within the timeframe of the assay. The p-values ($\geq$0.95) from statistical analyses suggest that the observed differences in cell

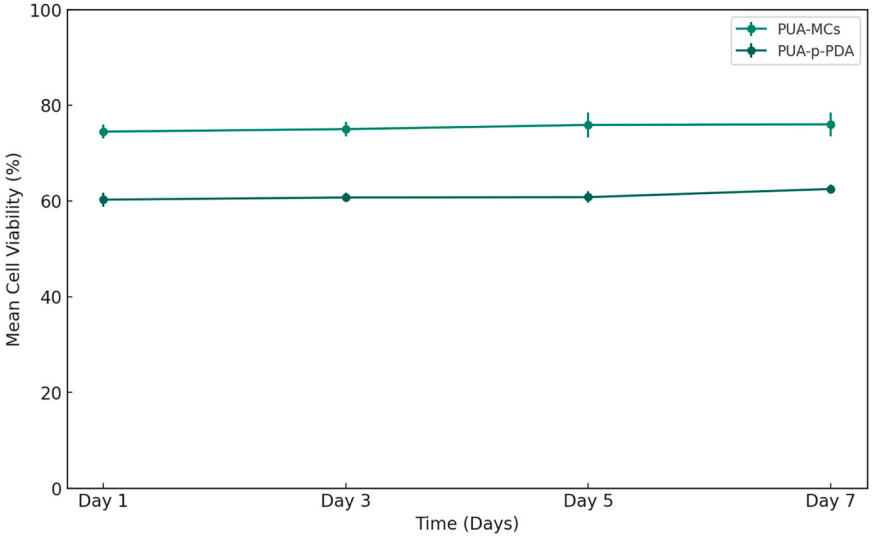

Fig. 6. Mean cell viability (%) over time for the two polyurea coating types.

viability over the days were not statistically significant, indicating a stable biocompatibility profile [27]. When incorporating potentially toxic substances such as tung oil into dental materials, the key lies in the formulation and processing that encapsulate or modify the toxic components to mitigate their harmful effects while retaining beneficial properties. For instance, in the case of PUA-MCs, tung oil could be chemically altered or cured as part of a polymer matrix that significantly reduces its bioavailability and thus its potential toxicity. This encapsulation ensures that the oil does not come in direct contact with tissues in a manner that would elicit the adverse effects commonly associated with its raw form.

Moreover, the controlled release characteristics and the chemically bound nature of tung oil in such polymer composites can further ensure that any residual toxicity is well below harmful levels, making it safe for medical and dental applications. The polymer matrix not only protects the patient from potential exposure to toxic substances but also leverages the durable and esthetically pleasing finish of tung oil, making it suitable for dental uses where both functionality and appearance are important [18]. The promising results of PUA-MCs in this study support its further investigation and potential adaptation into dental prosthetics, where improving the antimicrobial properties while ensuring minimal cytotoxicity is crucial. Future studies could expand on these findings by exploring long-term effects, combining these coatings with other antimicrobial agents, or testing in dynamic environments that mimic the oral cavity's conditions.

4.4. Antibiofilm evaluations

4.4.1. Biofilm quantification and structural analysis and viability of S. mutans cells

Evaluating biofilm formation on dental coating surfaces is pivotal for delineating their potential utility in oral healthcare. Utilizing the crystal violet staining assay, an established method for quantifying biofilms, we observed a 40 % reduction in biofilm biomass on coatings augmented with Tung oil compared to control samples. This marked decrease underscores the significant antimicrobial properties conferred by the Tung oil modification. Further insights were gained through confocal laser scanning microscopy, which enabled high-resolution visualization of the biofilms at 630× magnification [5,8]. The three-dimensional reconstructions of the biofilms on the Tung oil-modified surfaces showed considerably reduced thickness and notable structural anomalies. These anomalies included extensive voids and irregular biofilm mass distribution, suggesting an inhospitable environment for *S. mutans*, the bacterium primarily responsible for tooth decay and dental plaque [14]. The disrupted biofilm architecture implies that the Tung oil-infused polyurea coatings may disrupt critical biofilm development phases, such as initial adhesion and microcolony formation. This disruption is crucial in dental applications, as inhibiting biofilm maturation on tooth surfaces can curtail caries progression. Figure S2 illustrates the preliminary microscopic analysis of *S. mutans* biofilms cultivated on various dental coating formulations. Figure S2 **(a)** represents the baseline condition with minimal biofilm presence, showing sparse green fluorescence indicative of live bacteria with very few non-viable cells. Figure S2 **(b)** displays early signs of biofilm formation with an increased density of live bacteria (green) and emerging clusters of non-viable bacteria (red), suggesting initial biofilm disruption. Figure S2**(c)**shows advanced biofilm disruption with large areas of non-viable bacterial cells (red) dominating, highlighting the effective antimicrobial action of the coating. Figure S2**(d)**, which is similar to panel (a), with low biofilm density, demonstrating the coating's ability to inhibit biofilm redevelopment post-treatment. Figure S2**(e)** features moderate biofilm formation with better maintenance of bacterial viability compared to panel (b), indicating variable efficacy across different coating formulations. Figure S2**(f)** exhibits extensive biofilm formation with a significant presence of live bacteria, albeit with areas of disruption shown by patches of non-viable cells (red), indicating partial effectiveness of the antimicrobial coating. These images provide a visual quantification of the biofilm's structural integrity and the viability of *S. mutans* cells, showcasing the varying efficacy of Tung oil-enhanced polyurea coatings in preventing and disrupting biofilm formation. The differential staining vividly highlights areas of live and dead cells, serving as a crucial tool in assessing the antimicrobial performance of dental coatings under microscope-based preliminary studies. In this study, Tung oil-infused polyurea PUA-MC coatings consistently showed a higher ratio of nonviable *S. mutans* cells across multiple experimental iterations, highlighting the strong antibacterial action of the PUA-MC coating. This result was particularly encouraging for oral health, indicating that inducing S. mutans cell death can directly thwart dental plaque formation and its consequent cariogenic activity, which are primary factors in the onset of tooth decay.

4.4.2. Statistical analysis of biofilm and viability data

In the examination of biofilm viability and bacterial count reduction, the results derived from a detailed statistical analysis using two-way ANOVA underscored significant interactions between the type of dental coating, incubation temperature, and duration [28]. This analysis, rooted in rigorously collected data, revealed that the efficacy of the Tung oil-enhanced PUA-MC coatings in reducing bacterial viability is significantly influenced by environmental conditions, particularly temperature and incubation time. These findings are systematically presented in Fig. 7 derived from original data from Table S2, illustrating a broad spectrum of responses across varying conditions. The data consistently demonstrated that higher temperatures tend to augment the antimicrobial properties of the coatings. For instance, at a temperature of 35 ℃ over a 24-hour period, the PUA-MCs coatings showed a remarkable reduction in live S. mutans cells, achieving up to 29.31 % reduction. This pattern is indicative of the coatings' heightened bactericidal activity under elevated thermal conditions. Conversely, at lower temperatures and shorter time frames, the reduction percentages were generally lower, suggesting a temperature-dependent mechanism influencing the coating's efficacy. Similarly, the duration of exposure also played a crucial role in the effectiveness of the polyurea coatings. Longer exposure periods allowed for more significant reductions in viable bacterial counts, with extended periods of up to 192 h showing considerable reductions, particularly in the PUA-MCs coatings. The most potent antibacterial activity was observed at 40 ℃, where the reduction reached up to 26.17 % over 24 h, emphasizing the coatings' capacity to perform under sustained high temperatures. Moreover, the PUA-p-PDA coatings, while effective, typically exhibited slightly lower reduction percentages under the same experimental conditions, highlighting differences in the formulation's responsiveness to environmental factors. Notably, the PUA-p-PDA coatings achieved a maximum reduction of 29.39 % at 40 ℃ over 24 h, closely mirroring the highest efficacy observed with PUA-MCs coatings but with slightly less consistency across different temperatures and times.

The statistical significance of these observations, confirmed by p-values consistently less than 0.05, validates the robustness of the antimicrobial efficacy of the coatings. Such data not only reinforce the potential of these coatings in dental applications but also guide further optimization for enhanced performance. Furthermore, the responsiveness to temperature variation plays a critical role in the performance of these coatings. An increase in temperature generally enhances the efficiency of both coatings, possibly due to a thermally activated mechanism within the coatings or due to bacteria's increased vulnerability at elevated temperatures. The PUA-MCs coating, in particular, responds more dynamically to temperature fluctuations, showing notable improvements in efficacy at higher temperatures, peaking at 40°C. This enhanced temperature sensitivity suggests that PUA-MCs could be more effective under varying thermal conditions, a common scenario in clinical environments. When considering the overall performance, taking into account both time and temperature, PUA-MCs consistently surpasses PUA-p-PDA. This observation underscores the superior

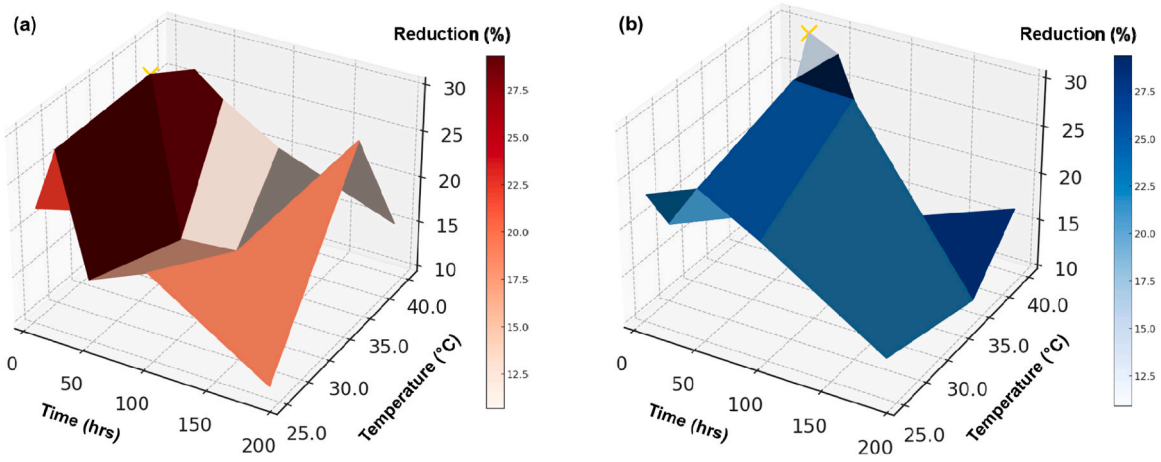

Fig. 7. 3D surface plots indicating potential antibacterial efficiency in viable *S. mutans* cell counts (a) PUA-MCs coating and (b) PUA-p-PDA coating.

antibacterial formulation of PUA-MCs, which could lead to more effective prevention of biofilm formation and bacterial proliferation on treated surfaces—a critical advantage in dental and other healthcare settings. Conclusively, the enhanced antimicrobial properties of the PUA-MCs coating are particularly pronounced at elevated temperatures and over extended periods, making it highly beneficial for dental applications where sustained antibacterial effects are crucial to preventing infections [25]. Conversely, while the PUA-p-PDA coating is effective, reaching similar levels of bacterial reduction may require longer durations or higher operational temperatures. This distinction is essential for the strategic development of medical coatings, emphasizing the need to tailor antibacterial activities to meet specific clinical requirements and enhance infection prevention strategies. The analysis reveals that both the type of coating and the operational conditions—temperature and time—are critical determinants of their effectiveness against bacterial proliferation. This insight is crucial for tailoring dental coatings to specific clinical needs, ensuring optimal performance in dynamic oral environments where fluctuations in temperature and exposure duration are common. These findings contribute significantly to the ongoing development and refinement of antimicrobial coatings, providing a strong empirical foundation for future research and application in clinical settings.

5. Conclusion

The research into Tung oil-infused polyurea microcapsules presents a significant advancement in dental materials, prioritizing both self-healing capabilities and stringent bioassay-based evaluations for toxicity and antibiofilm properties. This study has demonstrated that the integration of Tung oil not only enhances the inherent self-repair features of polyurea matrices but also effectively counters microbial colonization, which is crucial in the challenging environment of the oral cavity. The findings from the various tests conducted—ranging from cytotoxicity assays to mechanical durability and antimicrobial efficacy—point towards a promising future for Tung oil-modified polyurea coatings in dental applications. Specifically, the slight but consistent increase in cell viability over time with PUA-MCs coatings, as demonstrated by MTT assays, underscores a stable biocompatibility profile that is critical for dental materials. Despite the inherent toxicity concerns associated with Tung oil, its modified usage within polyurea microcapsules has shown to mitigate these risks effectively.

Furthermore, the study has explored the polyurea coatings' ability to autonomously repair physical damage and resist microbial growth, thereby enhancing the longevity and functionality of dental restoratives. This dual functionality is crucial in reducing the frequency of dental repairs and replacements, which are often costly and uncomfortable for patients. By extending the functional lifespan of dental prosthetics through innovative materials like Tung oil-infused polyurea, the study not only contributes to more sustainable dental practices but also enhances patient outcomes by minimizing the microbial risks associated with biofilms. The successful application of these coatings in dental materials could revolutionize the approach to dental restorative techniques, providing a model for future innovations in the field. It paves the way for further investigations into the integration of natural oils with medical-grade polymers, potentially opening new chapters in the synthesis of biomaterials designed for a range of healthcare applications beyond dentistry.

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CRediT authorship contribution statement

Borui Xu: Formal analysis, Validation, Writing – review & editing. **Peiyu Yuan:** Visualization, Validation, Resources, Investigation, Data curation. **Jiaqiao Zhong:** Investigation, Methodology, Validation. **Danqi Wang:** Writing – review & editing, Visualization, Validation, Investigation, Data curation. **YUANZHE LI:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **WanLuoh Choo:** Writing – original draft, Methodology, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2024.134529.

References

[1] A.M. Ferreira, P. Gentile, Editorial: biofunctional materials and coatings for orthopaedic and dental applications, Front Bioeng. Biotechnol. *11* (2023) 1203815, https://doi.org/10.3389/fbioe.2023.1203815.

[2] P. Cui, Q. Lin, D. Fang, L. Zhang, R. Li, J. Cheng, F. Gao, J. Shockey, S. Hu, S. Lü, Tung Tree (Vernicia fordii, Hemsl.) genome and transcriptome sequencing reveals co-ordinate up-regulation of fatty acid β-oxidation and triacylglycerol biosynthesis pathways during eleostearic acid accumulation in seeds, Plant Cell Physiol. *59* (10) (2018) 1990–2003, https://doi.org/10.1093/pcp/pcy117.

[3] S. Han, Y. Chen, S. Lyu, Z. Chen, S. Wang, F. Fu, Effects of processing conditions on the properties of paraffin/melamine-urea-formaldehyde microcapsules prepared by in situ polymerization, Colloids Surf., A. Physicochem. Eng. Asp. 585 (2020) 585.

[4] S. Ataei, S.N. Khorasani, R.E. Neisiany, Biofriendly vegetable oil healing agents used for developing self-healing coatings: a review, Prog. Org. Coat. *129* (2019) 77–95, https://doi.org/10.1016/j.porgcoat.2019.01.012.

[5] M. Hafezi, S. Nouri Khorasani, M. Zare, R. Esmaeely Neisiany, P. Davoodi, Advanced hydrogels for cartilage tissue engineering: recent progress and future directions, Polymers *13* (23) (2021), https://doi.org/10.3390/polym13234199.

[6] K.A. Althaqafi, J. Satterthwaite, N. Silikas, A review and current state of autonomic self-healing microcapsules-based dental resin composites, Dent. Mater. *36* (3) (2020) 329–342, https://doi.org/10.1016/j.dental.2019.12.005.

[7] Y. Guo, X. An, X. Qian, Mechanochromic self-healing materials with good stretchability, shape memory behavior, cyclability, and reversibility based on multiple hydrogen bonds, ACS Appl. Mater. Interfaces *15* (15) (2023) 19362–19373, https://doi.org/10.1021/acsami.2c19919.

[8] H. Ying, Y. Zhang, J. Cheng, Dynamic urea bond for the design of reversible and self-healing polymers, Nat. Commun. *5* (2014) 3218, https://doi.org/10.1038/ncomms4218.

[9] M.T. Lam, J.C. Wu, Biomaterial applications in cardiovascular tissue repair and regeneration, Expert Rev. Cardiovasc Ther. *10* (8) (2012) 1039–1049, https://doi.org/10.1586/erc.12.99.

[10] L. Yuan, T. Sun, H. Hu, S. Yuan, Y. Yang, R. Wang, C. Lyu, F. Yang, X. Lyu, Preparation and characterization of microencapsulated ethylenediamine with epoxy resin for self-healing composites, Sci. Rep. *9* (1) (2019) 18834, https://doi.org/10.1038/s41598-019-55268-7.

[11] N. Iqbal, M. Tripathi, S. Parthasarathy, D. Kumar, P.K. Roy, Polyurea spray coatings: tailoring material properties through chemical crosslinking, Prog. Org. Coat. *123* (2018) 201–208, https://doi.org/10.1016/j.porgcoat.2018.07.005.

[12] H. Li, Y. Cui, H. Wang, Y. Zhu, B. Wang, Preparation and application of polysulfone microcapsules containing tung oil in self-healing and self-lubricating epoxy coating, Colloids Surf. A: Physicochem. Eng. Asp. *518* (2017) 181–187, https://doi.org/10.1016/j.colsurfa.2017.01.046.

[13] C.A. Stewart, Y. Finer, Biostable, antidegradative and antimicrobial restorative systems based on host-biomaterials and microbial interactions, Dent. Mater. *35* (1) (2019) 36–52, https://doi.org/10.1016/j.dental.2018.09.013.

[14] Z.O. Oyman, W. Ming, R. v d Linde, Oxidation of drying oils containing non-conjugated and conjugated double bonds catalyzed by a cobalt catalyst, Prog. Org. Coat. *54* (2005) 198–204.

[15] P. Singh, A. Rana, N. Karak, I. Kumar, S. Rana, P. Kumar, Sustainable smart anti-corrosion coating materials derived from vegetable oil derivatives: a review, RSC Adv. *13* (6) (2023) 3910–3941, https://doi.org/10.1039/d2ra07825b.

[16] K. Mphahlele, S.S. Ray, A. Kolesnikov, Self-healing polymeric composite material design, failure analysis and future outlook: a review, Polymers *9* (10) (2017), https://doi.org/10.3390/polym9100535.

[17] S. Zechel, M.D. Hager, T. Priemel, M.J. Harrington, Healing through histidine: bioinspired pathways to self-healing polymers via imidazole¯metal coordination, Biomimetics *4* (1) (2019), https://doi.org/10.3390/biomimetics4010020.

[18] Q. Shi, W. Wu, B. Yu, M. Ren, L. Wu, C. Zhang, Preparation of ecofriendly water-borne polyurethane elastomer with mechanical robustness and self-healable ability based on multi-dynamic interactions, RSC Adv. *12* (54) (2022) 35396–35408, https://doi.org/10.1039/d2ra07000f.

[19] I.S. Vintila, J. Ghitman, H. Iovu, A. Paraschiv, A. Cucuruz, D. Mihai, I.F. Popa, A microvascular system self-healing approach on polymeric composite materials, Polymers *14* (14) (2022), https://doi.org/10.3390/polym14142798.

[20] J. Luo, T. Wang, C. Sim, Y. Li, Mini-review of self-healing mechanism and formulation optimization of polyurea coating, Polymers *14* (14) (2022), https://doi.org/10.3390/polym14142808.

[21] L. Zhang, X. Zhang, R. Wang, Y. Zhang, J. Wu, Z. Zhou, P. Yin, Research progress in boron-modified phenolic resin and its composites, Polymers *15* (17) (2023), https://doi.org/10.3390/polym15173543.

[22] A. Chen, S. Deng, J. Lai, J. Li, W. Chen, S.N. Varma, J. Zhang, C. Lei, C. Liu, L. Huang, Hydrogels for oral tissue engineering: challenges and opportunities, Molecules *28* (9) (2023), https://doi.org/10.3390/molecules28093946.

[23] L. Fang, J. Chen, Y. Zou, Z. Xu, C. Lu, Thermally-induced self-healing behaviors and properties of four epoxy coatings with different network architectures, Polymers *9* (8) (2017), https://doi.org/10.3390/polym9080333.

[24] Y.K. Song, H.W. Kim, C.M. Chung, Repeatable self-healing of a protective coating based on vegetable-oil-loaded microcapsules, Polymers *14* (10) (2022), https://doi.org/10.3390/polym14102013.

[25] E.E. Jaekel, S. Filonenko, Cationic CNC-stabilized Pickering emulsions of linseed oil for hydrophobic coatings, RSC Adv. *13* (25) (2023) 16860–16866, https://doi.org/10.1039/d3ra01412f.

[26] J. Chen, X. Zou, Self-assemble peptide biomaterials and their biomedical applications, Bioact. Mater. *4* (2019) 120–131, https://doi.org/10.1016/j.bioactmat.2019.01.002.

[27] T. Li, T. Zheng, J. Han, Z. Liu, Z.X. Guo, Z. Zhuang, J. Xu, A.B. Guo, Effects of diisocyanate structure and disulfide chain extender on hard segmental packing and self-healing property of polyurea elastomers, Polymers *11* (5) (2019), https://doi.org/10.3390/polym11050838.

[28] M. Samadzadeh, S.H. Boura, M. Peikari, A. Ashrafi, M. Kasiriha, Tung oil: an autonomous repairing agent for self-healing epoxy coatings, Prog. Org. Coat. *70* (4) (2011) 383–387, https://doi.org/10.1016/j.porgcoat.2010.08.017.