

Running title: Injectable polymer / ceramic nanocomposite hydrogels as pulp capping materials

INJECTABLE POLYMER / CERAMIC NANOCOMPOSITE HYDROGELS AS PULP CAPPING MATERIALS

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ABSTRACT

Introduction

The hybridization of polymers and ceramic nanoparticles in injectable hydrogels is a promising advancement in the field of dentistry. By incorporating hydroxyapatite at nanoparticle level it assures increased mechanical strength and biocompatibility. This novel approach not only enhances application in pulp chambers with irregular configurations but also increases biological activity and thereby stimulating tissue regeneration. The functional adaptability and long term stability of this material can be transformative in the field of dental materials, offering a wide opportunity to enhance the pulp capping treatment outcomes.

Aim

To synthesise injectable polymer/ceramic nanocomposite hydrogels and perform their characterisation and evaluation of their potential as pulp capping material.

Materials and Methods

The synthesis of PEG and PVA based hydrogels incorporated with hydroxyapatite nanoparticles were done. The mechanical properties of the same, injectability, in vitro biocompatibility using dental pulp stem cells were done. FTIR, SEM and contact angle analysis were used to characterise the materials.

Results

The homogeneous dispersion of hydroxyapatite inside the polymer matrix of the synthesized polymer–ceramic nanocomposite hydrogels demonstrated a well-defined nanoscale architecture. The successful integration of the ceramic phase into the hydrogel network is confirmed by this structural homogeneity. When evaluated in pulp cavity simulations, the hydrogels showed outstanding injectability in addition to their structural qualities. They demonstrated good handling qualities that are crucial for clinical operations by exhibiting easy flowability and adapt to confined areas.

Conclusions

The best features of both mechanical strength and biocompatibility are incorporated in advanced polymer–ceramic nanocomposite hydrogels. They are of particular interest as possible pulp capping materials because of this combination. The practical importance of these hydrogels is exhibited by their optimum synthesis and the beneficial results seen in several analyses. They demonstrate considerable promise in settings that are similar to practical use, not just limited to theoretical expectations. The ability of these materials to surpass existing restorative dental standards is what makes them so appealing. They may be crucial in determining the future of dental care due to their versatility, resilience, and capacity to promote regeneration.

Keywords: hydrogels, disease, polymers, stem cells, tissue engineering, regeneration, illness, health system.

How to cite this article: Vaishali B, Mohan A, Abhilasha, Bhargavi. Injectable Polymer / Ceramic Nanocomposite Hydrogels as Pulp Capping Materials. Int J Drug Deliv Technol. 2026;16(57s): 292-297. DOI: 10.25258/ijddt.16.57s.38

Source of support: Nil.

Conflict of interest: None.

INTRODUCTION :

In modern day dentistry, injectable hydrogels that incorporate polymers and ceramics have grown into a promising group of materials, particularly for pulp capping[1]. These materials constitute a significant breakthrough in the manufacturing of comprehensive dental biomaterials considering that they are designed at the nanoscale, offering a highly advanced integration of their individual elements[2]. Nanotechnology-based approaches have received considerable interest due to the constant demand for better restorative options. In this context, hydrogel based systems that integrate ceramics and polymers offer a well-balanced combination of biocompatibility and mechanical strength, which renders them appropriate for practical dental applications. A key aspect tucked away in the center of teeth, the dental pulp is vulnerable to damage or microbial attacks, requiring careful interventions to maintain its effectiveness. Pulp capping has long been employed as a therapeutic strategy for preserving pulp vitality following exposure[3]. The drawbacks of conventional pulp capping materials, including calcium hydroxide, have prompted the investigation of novel regenerative substitutes [4]. In such a search for improved dental biomaterials, injectable hydrogels have become a focal point due to their ease of application and their ability to adapt to varying cavity forms [5]. As a result of their intricate nanoscale structure, polymer/ceramic nanocomposite hydrogels act as a multi dimensional remedy compared to the traditional materials. [6][7]. The matrix supporting the dispersion of crystalline nanoparticles is composed of polymers owing to its flexibility and adaptability[8]. These ceramics offer composite mechanical strength and bioactivity as they are often composed of biocompatible components including hydroxyapatite. Besides imparting superior mechanical characteristics, the nanocomposite structure facilitates bioactive interactions at the oral tissue interface [9].

A significant aspect regulating the longevity and performance of dental restorations is mechanical strength. The required mechanical support might not be supplied by regular pulp capping materials. On the other hand, nanocomposite hydrogels possess superior mechanical properties attributed to the synergistic relationship of polymers and ceramics [15]. By functioning as reinforcements within the polymeric matrix, the ceramic nanoparticles improve the hydrogel and boost its capacity to sustain loads. This greater mechanical strength guarantees continued efficacy in clinical applications by contributing to the

restoration's overall durability [16]. The goal of the study is to analyse the injectable polymer / ceramic nanocomposite hydrogels as pulp capping agents.

MATERIALS AND METHODS :**Polymer Matrix and Ceramic Nanoparticles :**

Polyethylene glycol (PEG; molecular weight of 6,000 g/mol) was chosen as the key polymeric component given its excellent solubility and established biocompatibility. In order to ensure structural integrity to the hydrogel, polyvinyl alcohol (PVA) was employed as a secondary polymer. The ceramic component included hydroxyapatite (HA) nanoparticles that were produced via precipitation. The firmly established biocompatibility and bioactivity of HA formed the framework for this choice[1][19][14].

Solvents and Crosslinking Agents :

PEG was first dissolved in dimethyl sulfoxide (DMSO) to increase its solubility and achieve the desired consistency. PVA was dissolved in deionized water so that it will facilitate the diffusion of hydroxyapatite. N,N'-methylenebisacrylamide (MBAA) was utilized to improve its structural stability. PVA was crosslinked utilising glutaraldehyde, a bifunctional aldehyde that promotes covalent crosslinking throughout its matrix[1][23].

Initiators and Stabilizers :

Tetramethylethylenediamine (TEMED) and ammonium persulfate (APS) acted synergistically to trigger the polymerization of acrylamide into PEG, which aided in the crosslinking process. During the production of hydroxyapatite nanoparticles, polyvinylpyrrolidone (PVP) served as a stabilizer to guarantee uniform dispersion and prevent agglomeration[1][9].

Synthesis of Polymer/Ceramic Nanocomposite Hydrogels:**Preparation and Polymerization of PEG Solution :**

PEG was dissolved in DMSO at a concentration of 20% (w/v) while being constantly stirred to aid complete dissolution. MBAA was added to the PEG solution at a molar ratio of 1:100 (MBAA:PEG) as the crosslinking agent. To initiate polymerization process, a solution containing TEMED and APS initiators was added to the PEG solution. After rapidly stirring the reaction mixture to assure homogeneity, it was transferred into a mold and allowed to polymerize for 24 hours at normal room temperature[1][23].

Synthesis and Crosslinking of PVA-HA Composite and incorporation into PEG Matrix :

A 10% (w/v) solution was prepared by dissolving PVA in deionized water. PVP was used as a stabilizer in a controlled precipitation process to produce HA nanoparticles. Under continuous stirring, the resultant

HA nanoparticles were uniformly dispersed throughout the PVA solution. The crosslinking reaction was initiated by incorporating glutaraldehyde to the PVA-HA mixture at a molar ratio of 1:50 (glutaraldehyde:PVA). In order to ensure covalent bonding within the PVA-HA matrix, the crosslinking process was performed at room temperature and carried on for 12 hours. For the purpose of inclusion of the crosslinked PVA-HA composite within the pre-polymerized PEG solution, it was sectioned into appropriate dimensions. The PVA-HA composite was distributed evenly throughout the PEG matrix owing to the amalgamation, which was carried out by gentle stirring[9][14][21].

Final Polymer/Ceramic Nanocomposite Hydrogel Formation :

After being transferred into molds, the PEG and PVA-HA particulates were allowed to polymerize for another 24 hours at room temperature. In order to guarantee purity of the final product, the resulting nanocomposite hydrogels were thoroughly cleaned to eliminate any residual solvents or initiators.

Characterization Techniques :

Mechanical Testing :

The mechanical properties of the hydrogel were evaluated using a universal testing machine. Stress-strain curves were created by subjecting cylindrical samples to tensile and compressive tests at controlled speeds. For a complete mechanical characterization, parameters including elastic modulus, ultimate tensile strength, and compressive strength were obtained.

Injectability Assessment :

Injectability was measured by simulated pulp cavities that were designed to simulate the irregular morphologies found in clinical settings. By injecting the hydrogels into these models, their adaptability to complex cavity configurations could be tested both qualitatively and quantitatively.

Biocompatibility Studies :

The biocompatibility of hydrogel was evaluated by cell culture tests. After the incorporation of human dental pulp stem cells (DPSCs) onto hydrogel surfaces, live/dead staining along with specific markers were employed to monitor the viability, proliferation, and differentiation of the cells.

Statistical Analysis :

To ensure both statistical rigor and reproducibility, each experiment was carried out in triplicate. A specialized software was used to perform statistical analyses such as t-tests and analysis of variance

(ANOVA) to identify significant differences between experimental groups.

RESULTS :

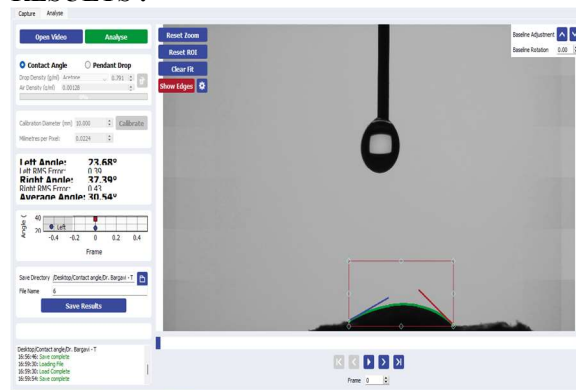


Figure 1 : Represents the contact angle of ceramic nanocomposites

The angle formed at the point of contact between the liquid drop and a solid surface is referred to as the contact angle, and it provides insight into surface energy, hydrophilicity, and possible interactions with nearby biological tissues. The morphology and chemical composition of the surface determine the contact angle. By introducing a droplet of a specific liquid to the hydrogel's surface and measuring the angle that yields, it is feasible to experimentally determine the contact angle. The contact angle is used to assess a material's hydrophilic surface property.

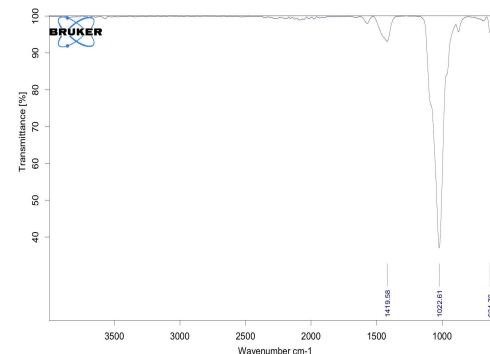


Figure 2 : Represents the Scanning Electron Microscopy (SEM) :

SEM was used to investigate the morphological aspects of the nanocomposite hydrogels. Following freeze-drying the sample to maintain its structural integrity, it was then sputter-coated with gold to improve its conductivity. A comprehensive examination of the nanoscale structure was rendered by SEM imaging at various magnifications. The substance is porous, flexible, and foldable, according to SEM morphology.

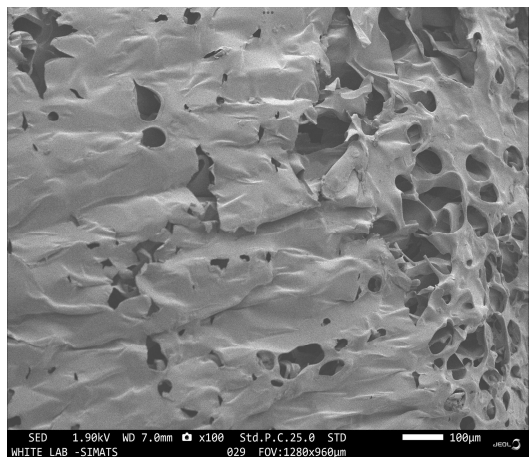


Figure 3 : Represents the Fourier transform infrared (FTIR)

The resultant polymer/ceramic nanocomposite hydrogels' functional groups and chemical bonds have been determined using FTIR. The crosslinking within the polymer matrix has been confirmed using FTIR. The presence of specific peaks associated with structural integrity of the hydrogels. FTIR can be utilized for quality assurance, ensuring that the synthesized hydrogels are void of impurities or residual solvents. The successful integration of these polymers into the nanocomposite hydrogels is proven by specific peaks in the FTIR spectrum that correspond to functional groups in these polymers.

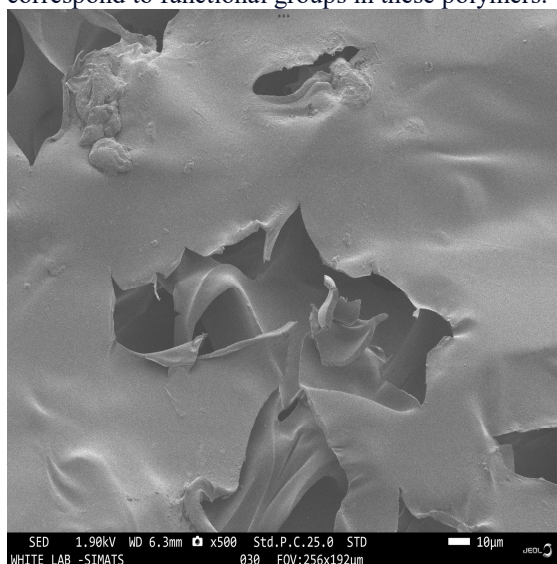


Figure 4 : Represents the FTIR Spectrum Showing Functional Group Identification and Chemical Composition

The interaction of infrared radiation with the sample is portrayed by the FTIR spectrum, making it possible to identify the sample's chemical composition and functional groups. The energy of absorbed infrared radiation is expressed by the wavenumber (cm^{-1}) on the x-axis, while the fraction of radiation transmitted through the sample is depicted by the transmittance (%) on the y-axis. The observed downward peaks indicate areas of diminished transmittance, indicating enhanced infrared radiation absorption as an outcome of molecular bond vibrational transitions.

Various functional group vibrations, such as C–H bending, C–O/C–N stretching, and possible metal–oxygen bonding, are responsible for the characteristic absorption bands that are seen at roughly 1419 cm^{-1} , 1022 cm^{-1} , and $600\text{--}650 \text{ cm}^{-1}$. These peaks confirm the structural composition and verify the presence of various chemical groups within it. In brief, the FTIR analysis is employed as a qualitative technique to confirm the efficacy and chemical integrity.

DISCUSSION :

The application procedure in dental procedures has been transformed by the innovative injectability of the nanocomposite hydrogels [10]. Since it is injectable, it can potentially be placed into pulp cavities with varying shapes, ensuring full coverage and tissue conformity. This feature bypasses the challenges presented by conventional materials, which may find it hard to conform to complex geometries, minimising their efficiency[11]. Biocompatibility is vital for the development of dental biomaterials, and polymer/ceramic nanocomposite hydrogels excel in this respect [12]. The specifically selected polymers offer little or no cytotoxicity and stimulate beneficial responses in the surrounding tissues. Furthermore, integrating naturally derived ceramic nanoparticles, like hydroxyapatite, improves bioactivity and thus provides an environment that is advantageous for tissue regeneration [13]. This is particularly crucial especially when it involves pulp capping, mainly because preserving the pulp's vitality and facilitating reparative dentinogenesis being the ultimate objectives[14]. Recent studies have shown that injectable polymer-ceramic nanocomposite hydrogels offer better controlled degradation, the ability to modulate the rate and extent of inflammation, antimicrobial properties, the capability to promote reparative dentin, and enhanced odontogenic differentiation, as compared to traditional pulp capping materials[19-23].

Dental pulp mesenchymal stem cells (DPCs), which are obtained from both young permanent and deciduous teeth, are distinctive by their capacity to possess neurogenic, osteogenic, chondrogenic, and adipogenic potential. This ability to adapt offers possibilities for tissue engineering, particularly for the creation of composite structures[17]. Hydrogels serve as a dynamic method to modify swelling rate, water content, degradation time, plasticity and hardness all of which are affected by factors such as pH, temperature, as well as polymer properties. Tissue engineering can be used to produce composite structures using inducible scaffolds and hard tissue filling materials enabling the repair and regeneration of refractory hard tissues [18].

Future Directions and Implications :

These comprehensive characteristics of the nanocomposite hydrogel render them desirable candidates for further therapeutic purposes. These are suitable for an array of dental applications besides pulp capping considering their adaptability , mechanical durability, and bioactivity. Their regenerative and biomimetic properties could also be used in the future for the engineering of the dentin–pulp complex and in regenerative dental therapies.

In addition, the capacity to alter the composition according to FTIR observations provides opportunities for customization, permitting it to be customized to specific patient needs and clinical requirements. While nanocomposite hydrogels move towards potential therapeutic uses, standardization and regulatory approvals become critical considerations. The flexibility and widespread use of such innovations in dental biomaterials are made possible by standardization processes that are influenced by the evidence of credible characterisation techniques.

CONCLUSION :

Injectable polymer/ceramic nanocomposite hydrogels have brought in a new era for pulp capping materials. Due to the nanoscale convergence of polymers and ceramics, these hydrogels provide an exclusive range of properties, from outstanding mechanical strength to good biocompatibility. Their injectability promises more flexibility to diverse pulp cavity shapes and further optimizes their application in dental operations. The incorporation of nanotechnology into dental biomaterials is anticipated to alter the standards of care in restorative dentistry as research in this specific subject advances, with polymer/ceramic

nanocomposite hydrogels at the forefront of this revolutionary journey.

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