Composites of Poly(ethylene glycol) and Hydroxyapatite: Dynamic Mechanical Study of the Modulus of Elasticity under Cryogenic Conditions

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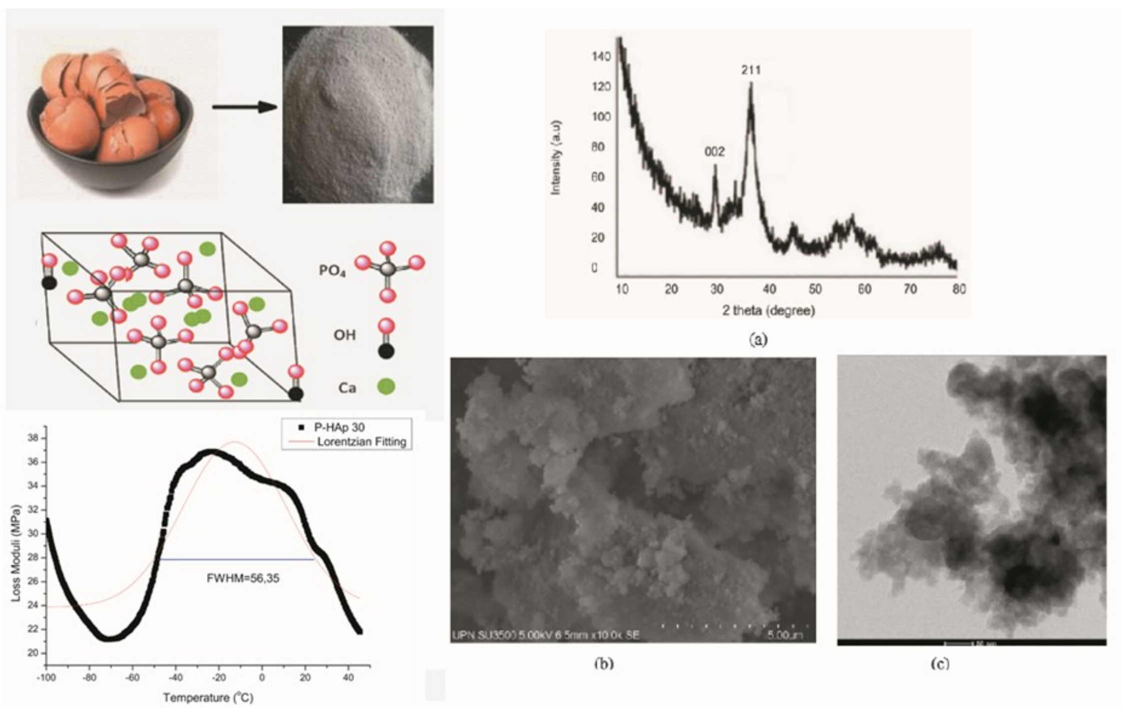
GRAPHICAL ABSTRACT



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The cryogenic mechanical behavior of polyethylene glycol (PEG) and hydroxyapatite (HAp) composites was studied using Dynamic Mechanical Analysis (DMA). The HAp was synthesized from chicken eggshells *via* a hydrothermal process, offering a sustainable, bio-derived source of calcium phosphate. The composites were fabricated through a wet mixing technique to ensure uniform distribution of HAp within the PEG matrix. Cryogenic characterization was conducted over a temperature range of minus 100 °C to 50 °C to evaluate the viscoelastic properties of the composites under extreme conditions. The results demonstrated a significant enhancement in the storage modulus (E'), with the 30 wt% PEG-HAp composite achieving a peak value of 1.128 GPa. This improvement is attributed to the effective impregnation and interfacial interaction between the PEG and HAp phases. These findings indicate the potential applicability of PEG/HAp composites in biomedical and cryogenic environments, although further studies are necessary to explore their specific functional roles in targeted applications. The study contributes to the advancement of biocomposite materials by elucidating the effects of cryogenic conditions on mechanical performance and supports the use of sustainable raw materials in composite fabrication.

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Keywords: Cryogenic; Dynamic mechanical analysis; Hydroxyapatite; PEG

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INTRODUCTION

The rapidly expanding field of biomedical engineering will require more advanced material implants as degenerative illnesses, accident rates, and the aging population increase (Datta *et al*. 2022; Bandyopadhyay *et al*. 2023). Material implants are crucial for restoring functionality and enhancing quality of life for people who have undergone surgery. However, selecting the appropriate biomaterials is essential, as it influences the implant's functionality as well as the patient's capacity for healing

(Eftekhar Ashtiani *et al*. 2021; Davis *et al*. 2022; Abraham and Venkatesan 2023). A major obstacle in the development of material implants is making sure that the material is biocompatible, or that it may safely interact with biological tissues without causing negative reactions (Ozturk *et al*. 2020; Deng *et al*. 2024; Singh *et al*. 2024). Conventional materials, such as polymers and metals, frequently have issues with long-term performance and integration with human tissue.

Hydroxyapatite (HAp) is widely recognized as the most common bioactive coating due to its natural occurrence in hard tissues and its ability to promote osseous integration. The HAp coating forms chemical bonds with human bone-like tissues, enhancing the adhesion of implants under functional conditions. However, despite these advantageous properties, Hap's brittleness and low bending strength currently limit its ability to meet the mechanical requirements of bone implants, thereby constraining its applications as a biomaterial. To address these challenges, various efforts have been made to synergistically combine HAp with other materials, including metals, ceramics, and polymers, to improve its mechanical properties and achieve performance levels comparable to those of human bone. One of the polymers suitable for use in biomaterials is PEG, which is known for its biocompatibility, hydrophilicity, flexibility, non-toxicity, and exceptional ductility and toughness (Fauziyah *et al*. 2017, 2019; Dhiflaoui *et al*. 2023). Incorporating PEG into HAp can regulate the particle size, crystal phase, and level of agglomeration of the HAp particles. In this study, the limitations of HAp were effectively mitigated by creating a composite with PEG (Aiza Jaafar and Zainol 2023; Sakinah *et al*. 2024).

Previous studies have investigated various characteristics of HAp/PEG composites, particularly their structural integration and thermal behavior. Zheng *et al.* (2021) demonstrated that PEG adsorbs onto the HAp surface *via* a direct impregnation process, achieving an encapsulation ratio close to 75%, which highlights the efficiency of PEG incorporation. Jamarun *et al.* (2023) analyzed the thermal degradation behavior of HAp-PEG composites using TGA-DTA, identifying 70 °C as the optimal degradation temperature and revealing PEG disintegration in the range of 176 to 306 °C. However, these studies were conducted under ambient or elevated temperatures. To date, no research has addressed the mechanical or structural stability of PEG-HAp composites under cryogenic conditions, which are relevant for biomedical scenarios involving low-temperature storage, transport, or surgical applications. Furthermore, while Iwamoto *et al.* (2021) observed that PEG molecular weight had minimal effect on cell adhesion to HAp ceramics, this finding has yet to be contextualized under cryogenic stress. Therefore, this study aims to fill the knowledge gap by evaluating PEG/HAp composite behavior under cryogenic conditions using dynamic mechanical analysis (DMA), a technique suitable for probing temperature-dependent mechanical responses

The Dynamic Mechanical Analysis (DMA) serves as a powerful and sensitive technique to evaluate the thermomechanical and viscoelastic properties of polymer-based composites across a wide temperature range, including sub-zero (cryogenic) conditions. Unlike conventional mechanical testing, DMA allows for real-time monitoring of material responses to oscillatory stress, enabling precise characterization of storage modulus, loss modulus, and damping behavior—parameters that are crucial for understanding how materials perform under mechanical load and thermal fluctuation. This makes DMA particularly suitable for investigating the stability and functional reliability of PEG/HAp composites when exposed to cryogenic environments, which are common in medical applications such as cryopreservation, low-temperature storage, or surgical procedures involving hypothermia. By exploring how cryogenic conditions alter the viscoelastic profile of these biomaterials, the study seeks to bridge a significant knowledge gap in their performance characterization. Ultimately, the findings aim to inform the design of more robust and reliable biomaterials for regenerative medicine and other biomedical fields.

EXPERIMENTAL

Materials

The compounds used in this study included PEG4000 ($HO(C_2H_4O)_nH$; ≥99% purity), which was acquired from Merck Schuchardt OHG located in Hohenbrunn, Germany (Merck Catalog 8.07490.1000). Sodium hydroxide (NaOH, 98% purity), phosphoric acid solution (H_3PO_4, 96%), and hydrochloric acid (HCl, 96% purity) were utilized for the coprecipitation and titration processes, respectively. Furthermore, domestic chicken eggshells were used as a calcium source (CaO of 73.65%) in the synthesis of hydroxyapatite, through a calcination process to form CaO which was then reacted with wet chemistry. The resulting HAp crystal structure is hexagonal, consisting of Ca^{2+} ions, PO_4^{3-} groups, and OH^- groups arranged in an orderly manner, as shown in Fig. 1.

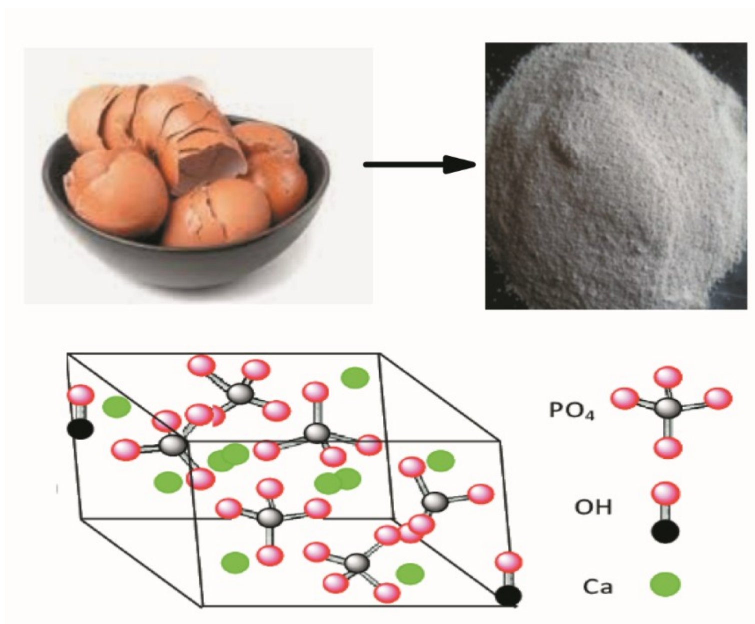

Fig. 1. The source of domestic chicken eggshell used in the production of HAp and its crystal structure

Hydroxyapatite Synthesis from Domestic Chicken Eggshells

First, the domestic chicken eggshells were cleaned with distilled water as part of the raw material preparation process. Next, the chicken eggshells were dried for five days until they were totally dry. Once the chicken eggshells had dried, they were pounded into flour using a mortar and pestle and sieved using a 100-mesh sieve. A storage box was filled with the ground eggshell flour.

The eggshell flour that was created in the previous step was calcined for 4.5 h and 6 h at 1000 °C in an electric furnace or furnace until it turned into CaO. Following the calcination procedure, the calcined chicken eggshells were sieved using a sieve before being weighed again.

The solutions that needed to be prepared were 1 M NaOH, 0.6 M H_3PO_4, and 1 M $Ca(OH)_2$ solutions. To make 200 mL of calcium hydroxide solution, 14.8 g of CaO (from chicken eggshells) was added to distilled water. To make 200 mL H_3PO_4 at 0.6 M, 8.1 mL of 85% H_3PO_4 and water were used.

Hydroxyapatite was synthesized from CaO (chicken eggshells) and phosphoric acid solution. The $Ca(OH)_2$ solution was mixed with H_3PO_4 solution at an addition rate of 5 mL/min; the mixing process was carried out until the H_3PO_4 solution ran out. During mixing, the suspension was stirred using a magnetic stirrer at a speed of 300 rpm. After the mixing process was complete, the suspension was heated at a temperature of 90 °C for 1.0 h. In this process, the pH of the solution was adjusted to reach a pH value of 11 using a NaOH solution. After the process was complete, the mixture was subjected to the aging process by cooling it at room temperature for 24 h. The precipitate produced from the aging process was then filtered. The filtered precipitate was then dried using an oven at a temperature of 200 °C for 2 h. To produce pure HAp, calcination was carried out at a temperature of 600 °C for 3 h.

PEG-HAp Composite Preparation

The preparation of the composite involved a wet mixing process of polyethylene glycol (PEG) and hydroxyapatite (HAp). Additionally, the amount of HAp incorporated into the PEG was varied in three different weight percentages of 10 wt%, 20 wt%, and 30 wt%. When using the wet mixing method, PEG 4000 was mixed while it is still in liquid form. At 60 ℃, mixing is accomplished by stirring at a speed of 200 rpm. Subsequently, the sample is printed with 1 cm × 5 cm dimensions and 0.2 cm thickness.

Characterization

The analytical methods and instruments utilized in this study were selected to comprehensively evaluate the structural, chemical, thermal, and mechanical properties of the PEG/HAp composites. X-ray Diffraction (XRD) analysis was conducted to evaluate the crystallinity and phase composition of the synthesized Hap, which is essential for understanding material stability and bioactivity using 10°-80° of 2θ.

Dynamic Mechanical Analysis (DMA) was conducted using a DMA/SDTA861e Mettler Toledo in tensile mode, following ASTM D5026 (2023). The temperature was ramped from −100 to 50 °C at a rate of 3 °C/min, to assess the viscoelastic behavior and thermal stability of the composites under cryogenic conditions, which is critical for biomedical applications involving low-temperature exposure.

Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Bruker Vertex 7.0v spectrometer in the range of 4000 to 400 cm^{-1} to identify functional groups and confirm the chemical bonding interactions between PEG and HAp within the composite matrix.

Scanning Electron Microscopy (SEM) (Carl Zeiss) was carried out at an accelerating voltage of 20 kV in secondary electron imaging mode, with magnifications ranging from 5,000× to 20,000×, to observe the surface morphology, particle dispersion, and homogeneity of the composite structure.

Transmission Electron Microscopy (TEM) analysis was performed using an FEI Tecnai-T20 operating in bright-field mode at 200 kV accelerating voltage and a camera length of 680 nm. This was used to further examine nanocrystals features and the interface between PEG and HAp at higher resolution.

Each of these methods was chosen to address a specific aspect of the material's performance and to support the overarching goal of characterizing PEG/HAp composites for use in biomedical applications, especially under cryogenic conditions.

RESULTS AND DISCUSSION

Crystal Characteristics

The crystalline structure of HAp, which was generated from domestic chicken eggshells, was evaluated using XRD analysis, which revealed unique features (Fig. 2a). The analysis showed that pure HAp had been formed (crystallinity of 85.2% and 14.8% amorphous) with the broadening of the main peak of HAp marker at 2θ ~30º and ~38º (corresponds to the PDF card number 01-072-1243) (Londoño-Restrepo *et al*. 2020; Liu *et al*. 2021). This relates to the space group P63/m and validates HAp creation.

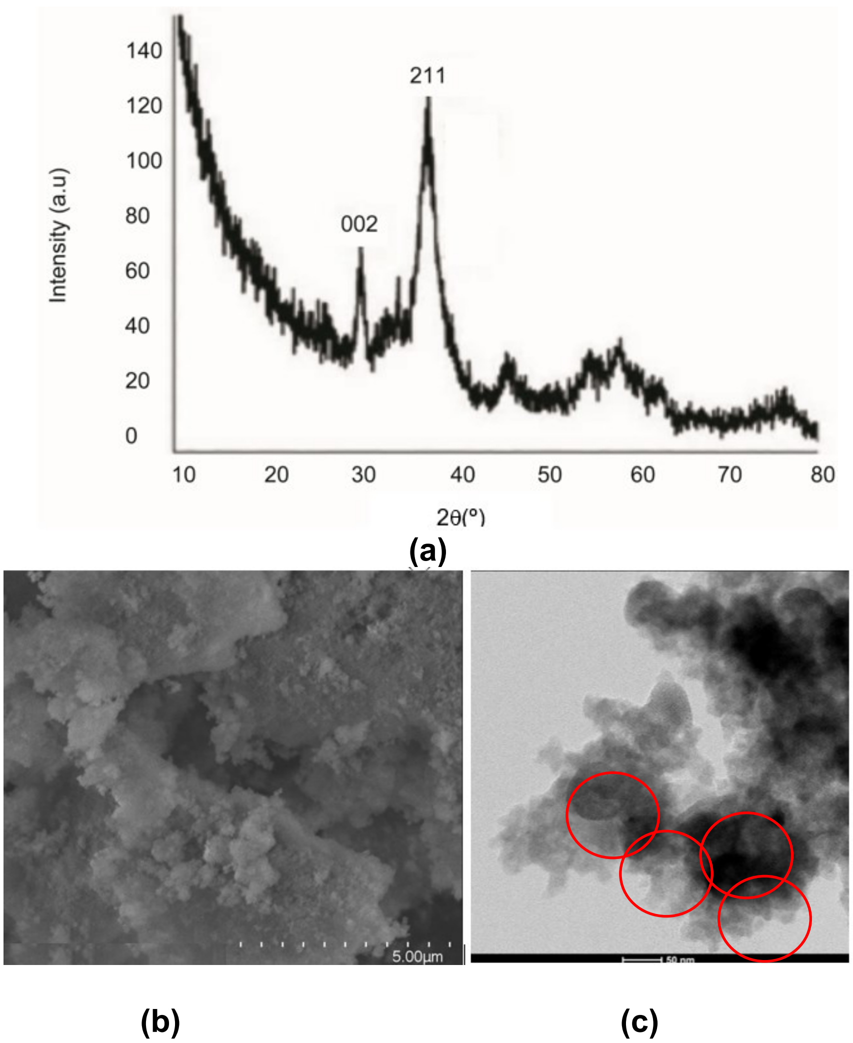

Fig. 2. (a) HAp diffraction pattern, (b) HAp particle morphology using SEM, and (c) HAp morphology dimensions using TEM

Although the morphology confirms that HAp particles were successfully formed through the hydrothermal method, SEM analysis (Fig. 2b) revealed regions with reduced homogeneity, indicating clustered particle distribution. Additionally, TEM analysis (Fig. 2c) supports the presence of nanocrystalline HAp exhibiting localized aggregation, which may lead to compromised load-bearing capacity. This potentially would affect the material's mechanical performance and biomedical applicability. Figure 2c reveals that the size of the crystals formed was nanocrystals (< 50 nm), but still there were some agglomerated clusters and some bigger crystalline material (100 to 130 nm, showed by red circles). The calcination process conducted at a temperature of 600 ºC promoted particle growth, enhancing the likelihood of adjacent particles merging to form larger particles (Arslan and Dogan 2018; Tang *et al*. 2020). To reduce the potential for agglomeration, surface modification is necessary (Ahangaran and Navarchian 2020; Manyangadze *et al*. 2020; Vandenabeele and Lucas 2020). Techniques such as polymer coating, surfactant-assisted dispersion, or ultrasonic treatment have been widely explored to improve the dispersion of nanoparticles within a matrix. These strategies work by reducing surface energy and preventing particle–particle attraction, which commonly leads to clustering. Improved dispersion not only enhances the mechanical homogeneity of the composite, but it also contributes to better biological performance, such as cell adhesion and proliferation, making the material more suitable for biomedical applications. However, this study did not implement such modifications.

Based on the description above, the HAp synthesized in this study showed a higher degree of crystallinity than previously produced commercial products (as determined by X-ray diffraction analysis), which generally have crystallinity in the range of 60% to 75%, depending on the synthesis method, calcination temperature, and source material used (Muralithran and Ramesh 2000; Dorozhkin 2010; Sadat-Shojai *et al.* 2013). In addition, TEM analysis showed that the particle size of the synthesized HAp was in the nanometer range (20 to 60 nm), which results in a high specific surface area. These physicochemical characteristics are known to enhance bioactivity, osteoconductivity, and drug adsorption capacity, thus greatly supporting applications in bone tissue engineering and drug delivery systems (Bose *et al.* 2013). This comparative analysis suggests that the synthesized HAp will have advantages over commercial products in terms of both structure and functionality.

Functional Groups from FTIR

Figure 3 shows the functional groups present in HAp, emphasizing the key molecular structures that contribute to its unique properties and behaviors. The FTIR absorption peaks of HAp are apparent around 3234 to 3482 cm^{-1}, which indicates the vibration peak of the hydroxyl group (–OH) (Hossain and Ahmed 2023); while the peaks around 430 to 630 cm^{-1} and 1030 to 1090 cm^{-1} are related to the vibration of the phosphate group ($–PO_4$) (Hossain and Ahmed 2023). These peaks, which can differ based on the synthesis technique employed, offer crucial information regarding the functional properties of HAp. Hydroxyl groups (-OH) are one of the key functional groups in HAp that improve its biocompatibility and ease interactions with biological tissues (Yuvaraj *et al*. 2021). These groups have the ability to generate hydrogen bonds, which enhance Hap's adherence to biological surfaces, which is an essential component of implant osseointegration. Phosphate groups ($–PO_4$) (Yazıcı *et al*. 2021) are also essential for maintaining structural stability and controlling the ion exchange properties needed for biological processes such as mineralization and bone regeneration. Calcium ions (Ca^{2+})

contribute to the structural integrity of HAp, maintaining the necessary cationic balance in the crystal lattice (Mondal *et al*. 2023), which in turn influences the material's mechanical properties and bioactivity. Additionally, some HAp samples may contain carbonate groups that can substitute for phosphate or hydroxyl groups, thereby enhancing the solubility and reactivity of the material for biological applications. Hap’s interactions with biological surroundings are greatly influenced by the configuration and kinds of its functional groups. Phosphoryl and hydroxyl groups encourage cellular and protein interactions, which improves integration with neighboring tissues. These functional groups also influence Hap’s mechanical characteristics, solubility, and bioactivity, which makes it a popular biomaterial for use in dental implants and bone transplants.

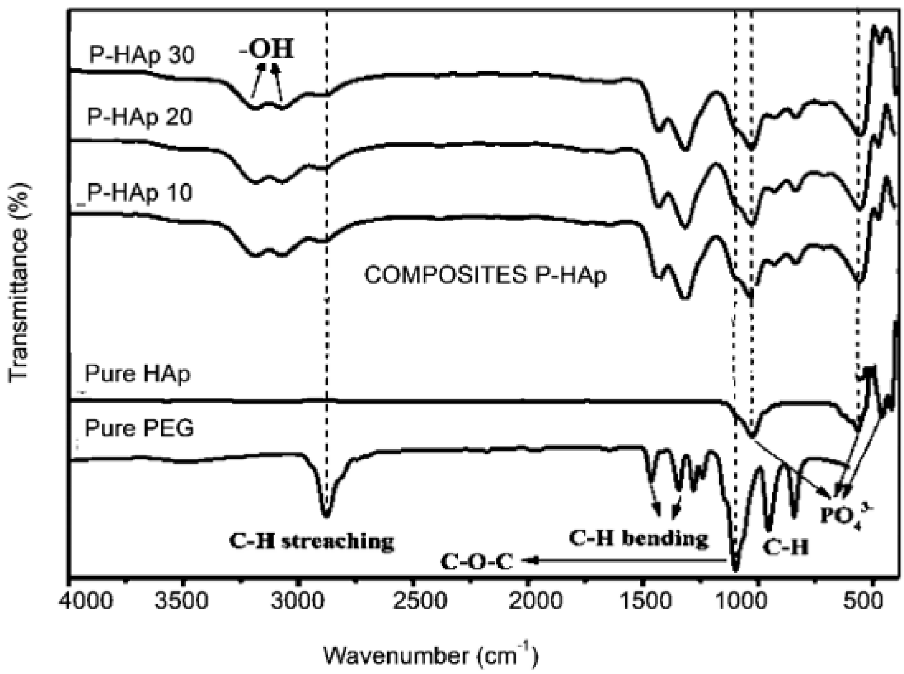

Fig. 3. Functional group analysis of HAp and PEG-HAp composite

Dynamic Mechanical Analysis

Table 1 summarizes the storage modulus (*E′*) and loss modulus (*E″*) values for PEG and various PEG-HAp composites.

Table 1. Storage Moduli (*E*‘) and Loss Moduli (*E*“) of PEG-HAp Composites at 100 ºC

Sample	*E*’ (GPa)	*E*” (MPa)
PEG	0. 975	65.75
P-HAp 10	1.032	26.74
P-HAp 20	1.098	23.98
P-HAp 30	1.128	31.23

These values are essential for understanding the mechanical behavior of the materials. The storage modulus (*E′*), expressed in gigapascals (GPa), indicates a material’s ability to store elastic energy and reflects stiffness, while the loss modulus

(E''), measured in megapascals (MPa), represents the ability to dissipate energy as heat during deformation, corresponding to viscous behavior.

As shown in Table 1 and Fig. 4, PEG alone exhibited the lowest stiffness (E' = 0.975 GPa) and the highest energy dissipation (E'' = 65.8 MPa), indicating its soft and flexible nature. Incorporating HAp increased stiffness while reducing energy loss. For example, PEG-HAp 10 showed an increased E' of 1.03 GPa and a reduced E'' of 26.7 MPa. This trend continued in PEG-HAp 20 (E' = 1.098 GPa, E'' = 23.98 MPa), reflecting an optimal balance between elasticity and damping. The PEG-HAp 30 sample demonstrated the highest stiffness, with an E' of 1.128 GPa, along with a moderate E'' of 31.23 MPa, indicating improved energy dissipation compared to other composites.

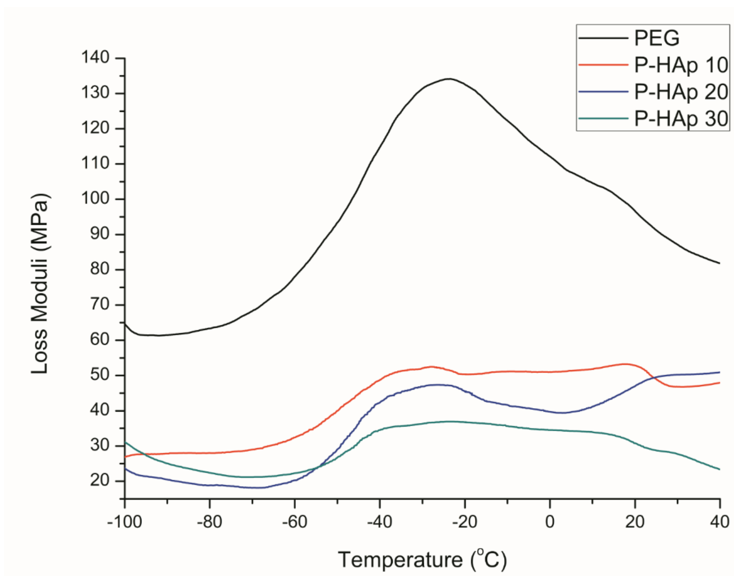

Fig. 4. Loss moduli (*E*") pattern from PEG_HAp composite using DMA

These improvements are attributed to the effective interaction between PEG and HAp during the mixing process. The adsorption of PEG onto HAp surfaces enhances interfacial adhesion, improving load transfer and mechanical performance (Bouazzi *et al*. 2023).

The mechanical enhancements observed in PEG-HAp composites can be attributed to the interfacial interaction between PEG and HAp, particularly the adsorption of PEG onto the HAp surface. This process occurs due to a combination of hydrogen bonding, van der Waals forces, and electrostatic interactions between the hydroxyl groups of PEG and the calcium or phosphate sites on HAp. These interactions facilitate uniform coating or anchoring of PEG chains onto the surface of HAp particles, which helps to prevent excessive agglomeration and promotes better dispersion of HAp within the polymer matrix.

Furthermore, the adsorbed PEG forms a semi-flexible interphase around the inorganic particles, improving stress transfer at the interface and enhancing mechanical reinforcement. This improved interfacial adhesion is particularly important during the direct impregnation process, where PEG infiltrates the porous structure of HAp, leading to composites with greater cohesion, improved stiffness, and controlled damping behavior (Bouazzi *et al.* 2023).

Figures 5(a)–5(c) present the viscoelastic analysis of PEG-HAp composites, in which the loss modulus (E'') data were fitted using the Lorentzian model to evaluate energy dissipation behavior over a range of temperatures. This approach allows the extraction of peak characteristics such as height and breadth, which reflect the material's damping performance and internal friction under stress. The Lorentzian model yielded good fitting accuracy for PEG-HAp composites with higher PEG content, particularly at 30 wt%, indicating a consistent viscoelastic response in these formulations.

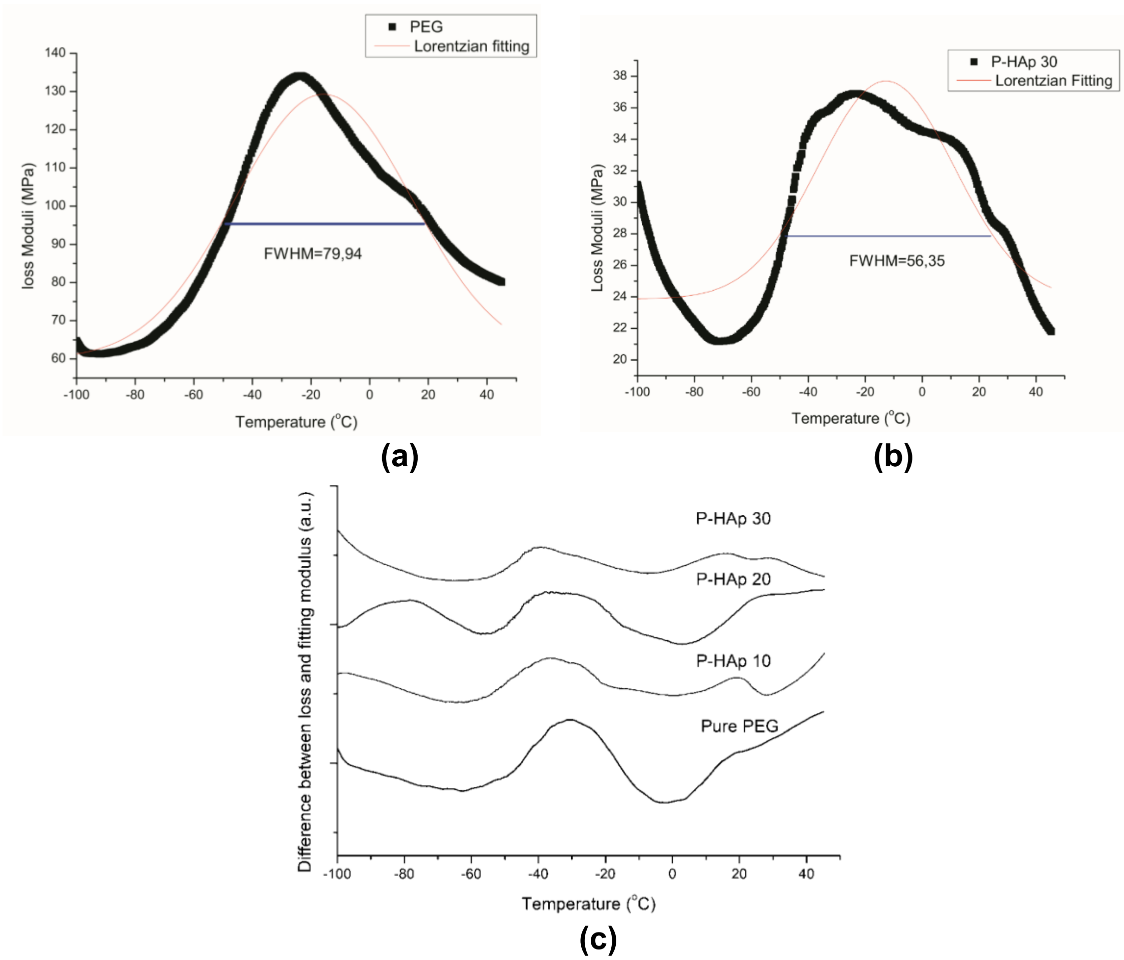

Fig. 5. Lorentzian fitting loss moduli of (a) pure PEG, (b) PEG-HAp composite, and (c) the difference between the loss moduli pattern resulting from the measurement and the Lorentzian fitting

However, for samples containing less than 30 wt% PEG, the model showed significant deviations from the experimental data. This poor fit may stem from uneven dispersion of PEG within the HAp matrix, resulting in localized regions with insufficient polymer content to dominate the damping behavior. Additionally, morphological factors, such as particle agglomeration and inhomogeneous phase distribution, could introduce mechanical irregularities that reduce the model's predictive accuracy. It is also possible that the limited viscoelastic contrast at lower PEG contents produces flatter or less distinct peaks, making Lorentzian fitting less effective in capturing the true thermomechanical profile. These factors collectively challenge the applicability of the Lorentzian model to low-PEG composite systems.

Figure 6 presents loss moduli (*E*") values and full width at half maximum (FWHM) for PEG and various concentrations of PEG-HAp composites, all measured at -100 °C. The PEG showed a *E*" of 65.8 MPa and a FWHM of 79.9, indicating its strong energy dissipation capabilities. In contrast, PEG-HAp 10 exhibited a drop in *E*" to 26.7 MPa and a lower FWHM of 54.8, suggesting enhanced stiffness but reduced energy dissipation. PEG-HAp 20 continues this trend with a further decline in *E*" to 24.0 MPa and a substantial increase in FWHM to 120.30, reflecting changes in viscoelastic behavior due to structural interactions. PEG-HAp 30 shows a recovery in *E*" to 31.2 MPa and a FWHM of 56.4, indicating that an optimal concentration of hydroxyapatite improves energy dissipation while balancing stiffness and flexibility.

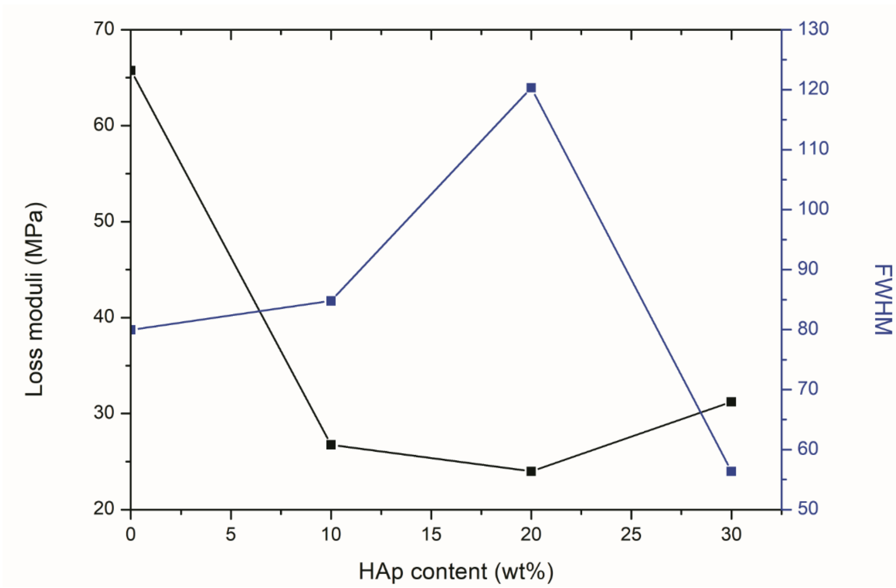

Fig. 6. Relationship between loss moduli and peak width (FWHM) of P-HAp composites

When thermoplastic polymer composites are subjected to extremely low temperatures (*e.g.*, –100 °C), they undergo significant changes in physical and mechanical behavior. One prominent effect is an increase in stiffness and tensile strength, which can be attributed to the reduced mobility of polymer chains at cryogenic conditions. For instance, studies have reported that the storage modulus of polyethylene-based composites can increase by up to 200% when cooled from room temperature to –100 °C (Chen *et al.* 2021). However, this improvement in strength is often accompanied by a decline in ductility and energy absorption, leading to increased brittleness, which raises concerns for impact resistance and structural reliability (Kim *et al.* 2022).

Furthermore, phase transitions may occur under cryogenic exposure, where polymers shift from an amorphous to a more ordered or crystalline configuration, impacting thermal conductivity and heat capacity (Barra *et al.* 2023). Dimensional changes, such as shrinkage, have also been observed, with typical linear contraction values reaching 0.3 to 1.2%, depending on the composite composition and filler content. These alterations may compromise the structural fit and functionality of components in precision applications. Long-term exposure to such low temperatures can also cause microcracking or interfacial debonding, accelerating the degradation of mechanical properties and reducing the service life of the material (Deng *et al*. 2024).

CONCLUSIONS

1. This study emphasized the structural and thermomechanical performance of hydroxyapatite (HAp) and its PEG-based composites, underscoring their relevance in biomedical material development. The presence of hydroxyl (-OH) and phosphate (-PO_4^{3-}) groups support bioactivity and osseointegration, while calcium ions contribute to mechanical reinforcement by stabilizing the crystal lattice. Additionally, carbonate substitutions, confirmed by FTIR analysis (with peaks at ~1410 cm^{-1} and 873 cm^{-1}), enhance the resemblance of synthetic HAp to natural bone mineral, improving resorption behavior and biological acceptance. The synthesized HAp in this study showed a crystallinity of 85.2%, exceeding typical commercial ranges (60 to 75%), which suggests improved mechanical stability and thermal resistance.
2. Dynamic mechanical analysis (DMA) revealed that PEG-HAp 30 exhibited the highest storage modulus (1.13 GPa) and moderate loss modulus (31.2 MPa), reflecting an optimal balance between stiffness and energy dissipation. At –100 °C, the composite's stiffness increased while brittleness decreased, particularly in samples with higher HAp content. This behavior supports their use in load-bearing, cryogenic, or high-precision biomedical applications, such as dental implants and orthopedic scaffolds.
3. Compared to traditional polymeric or ceramic biomaterials, PEG-HAp composites offer greater structural tunability, enhanced interfacial bonding, and superior cryo-mechanical resilience. The PEG matrix provides flexibility and processability, while HAp imparts bioactivity and stiffness, making these composites highly adaptable for next-generation regenerative therapies.

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