

## **SURFACE MODIFICATION OF HYDROXYAPATITE AND ITS EFFECT ON PLA COMPOSITES PREPARED BY CASTING**

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### **ABSTRACT**

Developing polymer–ceramic composites with controlled properties is essential for optimizing functional films for coatings and flexible devices. This study investigated poly(lactic acid) (PLA) films reinforced with hydroxyapatite (HA) at 5, 10, and 20 wt%, including HA surface-modified with PLA oligomers (Mw 2000), to evaluate how filler concentration and surface modification influence mechanical, thermal, and surface properties. Results show that surface-modified HA improves particle dispersion and interfacial adhesion, producing films with higher stiffness and hardness, particularly at 20 wt% HA modified, while crystallinity peaks at low HA concentration (5 %). Surface modification also generates rougher, more hydrophilic surfaces, enabling control over film topography and functional properties. Overall, the study demonstrates that HA incorporation and surface modification significantly affect the mechanical, thermal, and surface properties of PLA films. These findings provide insights into polymer–ceramic interactions in model film systems, highlighting strategies to optimize particle dispersion, interfacial adhesion, and surface functionality. Furthermore, this study shows that tuning HA concentration and surface chemistry is an effective strategy to optimize mechanical and surface properties of PLA films, providing guidance for the design of advanced functional materials.

**Keywords:** PLA; hydroxyapatite; composite films; surface modification; functional surfaces.

### **1 Introduction**

Poly (lactic acid) (PLA) is a prominent biodegradable and biocompatible aliphatic polyester widely employed as a pivotal model polymer in biomedical and materials research ((1), (2)). Its favorable mechanical properties and ease of processing establish it as a versatile platform for fundamental studies on polymer–ceramic composites.

Despite these advantages, PLA exhibits inherent limitations, including moderate stiffness, low toughness, and limited bioactivity (3). To enhance performance, PLA is frequently reinforced with bioactive ceramics such as hydroxyapatite (HA), the main mineral component of bone (4). The incorporation of HA acts as a rigid particle, increasing stiffness and hardness, but the final performance depends critically on achieving homogeneous dispersion and strong interfacial adhesion to prevent stress concentrations ((5), (6.))

To overcome compatibility issues, surface modification of HA is proposed. Functionalizing HA with oligomeric PLA chains enhances particle dispersion, reduces agglomeration, strengthens interfacial adhesion, and facilitates efficient load transfer, which also influences thermal transitions and surface characteristics ((6), (7)).

PLA films serve as an ideal experimental platform for systematically evaluating these effects, allowing controlled study of particle distribution and mechanical performance (8). The particle size of the HA filler is crucial, as it affects the surface area available for interaction and the potential for large particles to act as stress concentrators, thus reducing ductility and tensile strength.

The thermal properties (studied by DSC) reveal how HA and its modification influence crystallization behavior ( $T_g$ ,  $T_c$ ,  $T_m$ ). HA can act as a heterogeneous nucleating agent at low concentrations, while higher content may restrict chain mobility (9). Furthermore, surface properties like roughness and wettability are critical, as HA incorporation alters topography, and surface modification promotes uniform particle dispersion ((10), (11)).

The mechanical characterization via tensile testing and Vickers hardness provides complementary data on stiffness, strength, ductility, and resistance to localized deformation. Microstructural features, such as particle dispersion and interfacial quality, are observed using optical microscopy and SEM, linking microstructure to macroscopic performance ((12), (13)).

The objective of this study was to systematically evaluate how HA concentration (5, 10, and 20 wt%) and surface modification (using PLA-oligomer-modified HA) influence the mechanical, thermal, and surface properties of PLA films. By correlating morphological characteristics with mechanical and thermal behavior, this work provides fundamental insights into the design of polymer–ceramic model films, aiming to identify conditions that optimize reinforcement, surface uniformity, and structural integrity.

## 2 Materials and methods

**2.1. Sample Preparation:** PLA films reinforced with hydroxyapatite (HA) at 5, 10, and 20 wt%, including HA surface-modified with PLA oligomers (MW 2000), were prepared by the solvent casting method. PLA was dissolved in chloroform under continuous stirring until a homogeneous solution was obtained. Subsequently, HA or surface-modified HA was added gradually to the PLA solution, and the mixture was stirred until complete dispersion of the particles was achieved. The resulting suspension was poured into Petri dishes and dried in an oven at 40 °C for 24 hours to form uniform films. After drying, the films were carefully removed, cut into standardized dimensions, and conditioned for mechanical, thermal, and surface characterization.

**2.2. Particle size:** The particle size distribution of the samples was determined by Laser Diffraction (LD) using a Horiba Partica LA-950 analyzer in dry dispersion mode. All particle size parameters were calculated assuming a spherical shape. The following metrics were obtained directly from the instrument's software: particle volume distribution percentage,  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$ , as well as the De Brouckere mean diameter ( $D_{4,3}$ ) and the mode. Measurements were performed in duplicate, and the results are presented as the mean  $\pm$  standard deviation.

**2.3. Mechanical Testing:** Tensile tests were conducted on a universal testing machine (Instron 5967) at room temperature. Film specimens were tested at a crosshead speed of 1 mm/min according to ASTM D882. The elastic modulus, tensile strength, and strain at break

were recorded. Three replicates per condition were analyzed, and average values were reported.

**2.4. Differential Scanning Calorimetry (DSC):** Thermal properties were analyzed using a TA Instruments DSC Q2000. Samples of ~5–10 mg were placed in aluminum pans and heated from 25 °C to 200 °C at a rate of 10 °C/min under nitrogen atmosphere. Glass transition ( $T_g$ ), crystallization temperature ( $T_c$ ), melting temperature ( $T_m$ ), and percent crystallinity were determined from the resulting thermograms.

**2.5. Surface Roughness Analysis:** Surface roughness was evaluated using a Zygo NewView 7100 optical profilometer. Parameters including average roughness ( $R_a$ ), root mean square roughness ( $R_q$ ), Peak Density, Valley Density, and PV (Peak-Valley) were obtained at multiple points per surface. Results were averaged for each sample. Changes in roughness indicate morphological alterations due to particle incorporation and surface modification.

**2.6. Static Contact Angle Measurement:** Static contact angle with distilled water was measured on both surfaces (smooth and rough) of the films using a Goniometer Firstn Angstrom – Model FTA100. Approximately 1  $\mu$ L droplets were applied, and five measurements per sample were recorded to obtain average values. A decrease in contact angle indicates an increase in surface hydrophilicity.

**2.7. Vickers Hardness Test:** Vickers hardness was measured exclusively on the smooth surface using a Shimadzu HVM-G21DT durometer with an HV0.05 force (490.3 mN) applied for 15 seconds. Five indentations were made per sample, and average values were reported to assess structural integrity and mechanical resistance.

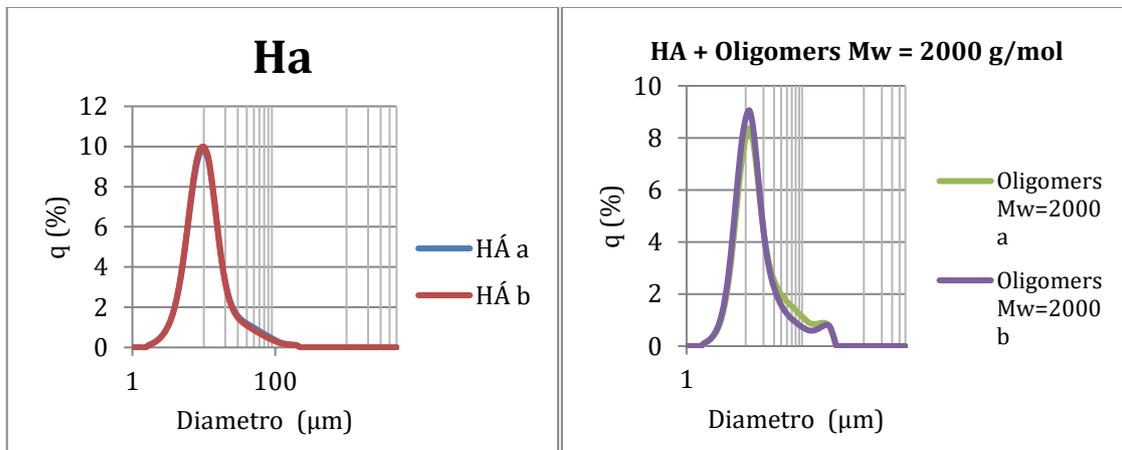
**2.8. Optical Microscopy (ZEIS):** Morphological changes and particle dispersion were observed using a ZEISS A1 optical microscope at 10X magnification. Representative digital micrographs were obtained and processed with ImageJ software (version 1.53) using thresholding and area measurement tools to quantify particle size, count, and uniformity of distribution.

**2.9. Scanning Electron Microscopy (SEM):** Surface morphology of the films was analyzed using a Quanta FEG 250 field emission scanning electron microscope (FE-SEM). Samples were sputter-coated with a thin gold layer (~5 nm) to ensure conductivity. Micrographs were acquired at magnifications ranging from 100 $\times$  to 1000 $\times$  using the high-resolution electron beam, allowing detailed evaluation of particle dispersion, surface texture, and interfacial adhesion between PLA and HA. The SEM's field emission gun provided enhanced resolution and imaging of surface features with minimal charging effects.

### 3 Results

**3.1 Particle size:** The particle size and its distribution are fundamental properties that influence the physical, mechanical, and processing characteristics of composite materials. For polymer-ceramic composites, these parameters are critical for understanding how the filler disperses within the matrix and how it ultimately affects the composite's overall performance. This section details the analysis of the particle size distribution of the

hydroxyapatite (HA) filler, both in its pristine form and after surface modification with PLA oligomers. The measurements were performed in duplicate to assess the reproducibility and observe the behavior of the samples (a,b)



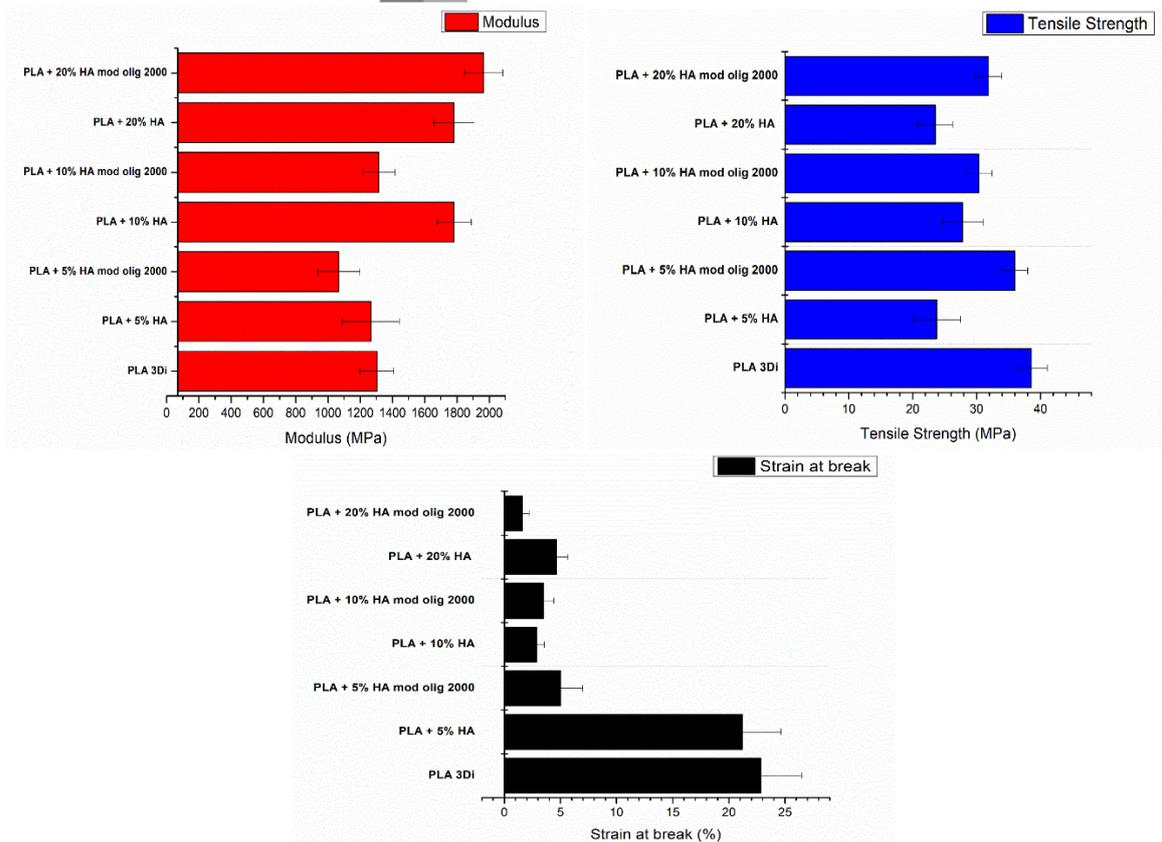
**Figure 1.** Particle Size Distribution of HA Before and After Surface Modification with PLA2000 Oligomers.

The surface modification of hydroxyapatite (HA) with PLA 2000 oligomers did not significantly change the primary mean particle size ( $\approx 10 \mu\text{m}$ ). However, this process led to a broader particle size distribution, characterized by the appearance of secondary populations ranging from 100 to 1000  $\mu\text{m}$ , indicating partial agglomeration.

This agglomeration is attributed to a decrease in the surface energy of the particles after oligomer coating. The resulting reduction in affinity for the dispersing medium promotes stronger particle-particle interactions (binding between particles) rather than interactions with the surrounding fluid.

The results suggest that the PLA2000 modification preserves the primary HA core but facilitates the association between functionalized surfaces, creating heterogeneity in the distribution. This tendency to form agglomerates is identified as a critical factor that must be considered during subsequent dispersion into the polymer matrix, as it will directly influence the composite's homogeneity and microscopic interaction.

**3.2 Mechanical properties:** The mechanical tests of PLA composites reinforced with different concentrations of hydroxyapatite (HA) and surface modified with 'olig 2000' are summarized in Table 1. The results detail the impact of reinforcement on the material's elastic modulus, tensile strength, and strain at break.



**Figure 2.** Elastic Modulus, tensile strength and strain at break of PLA Composites with Different Concentrations and Modifications of HA.

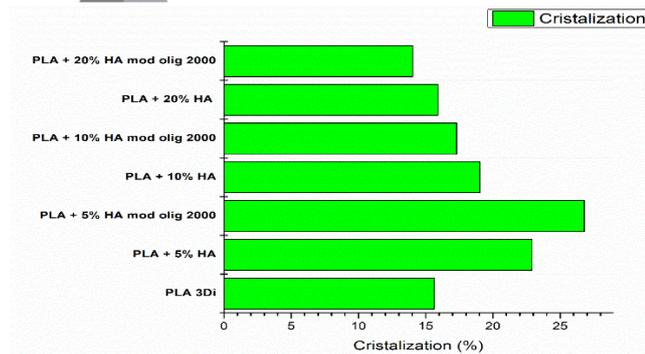
The incorporation of hydroxyapatite (HA) into the PLA matrix results in a consistent increase in the Elastic Modulus, confirming the reinforcement effect of rigid ceramic particles. The highest modulus value (1965 MPa) was achieved by the film containing 20% oligomer-modified HA, suggesting that surface functionalization optimizes interfacial adhesion and promotes more efficient load transfer.

Tensile Strength follows an overall decreasing trend due to stress concentration around the rigid particles, which act as crack initiation sites. However, the 20% oligomer-modified HA composite exhibited the highest tensile strength among all HA-containing formulations. This is attributed to the modification strengthening the interfacial region, mitigating stress localization, and distributing the load more evenly.

Strain at Break (ductility) is significantly reduced upon HA addition, an effect consistent with the restricted mobility and plastic deformation of the PLA chains imposed by the rigid filler. This loss of ductility is most severe at high concentrations.

In conclusion, HA incorporation enhances stiffness but compromises ductility. Crucially, the HA modification with oligomers partially offsets the loss in tensile performance by improving interfacial compatibility, achieving a better balance between reinforcement and the maintenance of structural integrity.

**3.3 Thermal properties (DSC):** The results of the differential scanning calorimetry (DSC) analysis, presented in Table 2, reveal how the addition and surface modification of hydroxyapatite (HA) affect the thermal structure and crystallinity of the PLA matrix.



**Figure 3.** Percentage Crystallization of PLA Composites with Different Concentrations and Modifications of HA

The Glass Transition Temperature ( $T_g$ ) (average  $\sim 60^\circ\text{C}$ ) and Melting Temperature ( $T_m$ ) (average  $\sim 176^\circ\text{C}$ ) remained remarkably stable across all films. This indicates that neither the incorporation of HA nor its surface modification significantly impacts the mobility of PLA chains in the amorphous phase or the material's fundamental crystalline structure. Conversely, the Crystallization Temperature ( $T_c$ ) was observed to be slightly higher in HA-containing films, suggesting that HA particles may physically hinder polymer chain organization in the melt, thus requiring higher temperatures to initiate the crystallization process.

Crystallinity exhibited a complex, concentration-dependent behavior. At low HA content (5%) in particular, the particles effectively served as heterogeneous nucleation sites, which promoted chain organization and led to a noticeable increase in crystallinity (22.92%) for unmodified HA). Surface modification with oligomers further amplified this effect, achieving the highest observed crystallinity (26.79%). However, at high HA content (20%), crystallinity decreased to values similar to pure PLA. This reduction is primarily attributed to the restricted chain mobility caused by the dense filler, which physically limits crystal growth and counteracts the nucleating effect. In summary, the DSC results underscore that low concentrations of HA, especially when surface-modified, significantly enhance PLA crystallinity, while high loadings may prove detrimental by physically impeding polymer chain motion, highlighting the need to optimize both filler content and surface chemistry.

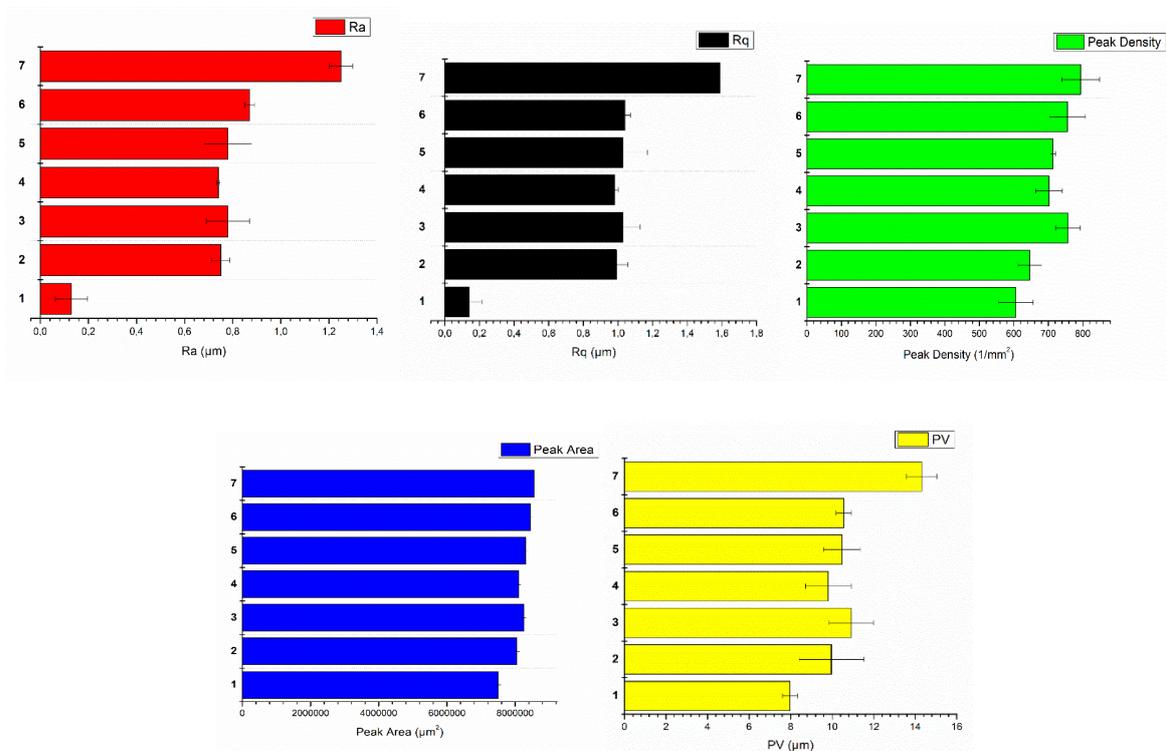
**3.4 Surface Roughness:** Surface roughness is a critical factor in the performance of polymer–ceramic films, as topography directly influences interactions with the surrounding environment. Five parameters were analyzed:

1. **Ra (Average Roughness):** The arithmetic mean of the deviations of the roughness profile. Ra reflects the overall surface roughness. An increase in Ra indicates that HA addition has made the surface generally rougher, providing more sites for potential interactions.
2. **Rq (Root Mean Square Roughness):** The root mean square of the deviations from the mean line. Rq is more sensitive to extreme peaks and valleys than Ra, highlighting pronounced topographical features created by HA particles.
3. **Peak Density:** The number of peaks per unit area. Higher peak density indicates a more textured surface, with more sites available for polymer–particle interactions or functionalization.

4. **Peak Area:** The total area of all peaks in the roughness profile. An increase in peak area shows a larger effective surface for interactions, demonstrating that the modification enhances the functional surface properties of the films.
5. **PV (Peak-to-Valley):** The vertical distance between the highest peak and lowest valley. Higher PV values confirm the presence of pronounced topographical features

**Table 1.** PLA Composite Sample Coding

|                                |   |
|--------------------------------|---|
| PLA 3Di                        | 1 |
| PLA 3Di + 5% HA                | 2 |
| PLA 3Di + 5% HA mod olig 2000  | 3 |
| PLA 3Di + 10%HA                | 4 |
| PLA 3Di + 10% HA mod olig 2000 | 5 |
| PLA 3Di + 20%HA                | 6 |
| PLA 3Di + 20% HA mod olig 2000 | 7 |



**Figure 4.** Surface Roughness Parameters (*Ra*, *Rq*, Peak Density, Peak Area, and PV) for the PLA Composites

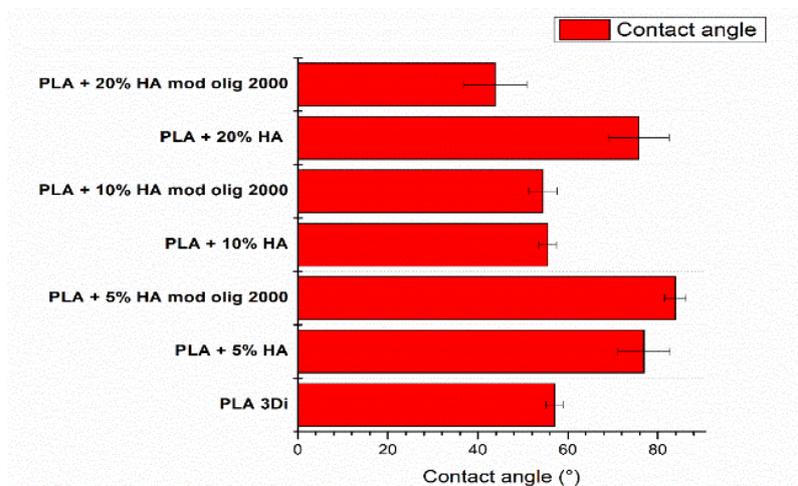
The observed increase in surface roughness is attributed to the inorganic nature of hydroxyapatite (HA) particles. During film fabrication, HA particles, being more rigid than the PLA matrix, do not deform uniformly. Instead, they protrude from the polymer surface, acting as topographical nucleation sites and creating measurable peaks and valleys.

Ra (Average Roughness), Rq (Root Mean Square Roughness), and PV (Peak-to-Valley) values increased substantially with HA incorporation; for instance, Ra rose from  $0.129 \mu\text{m}$  for pure PLA to  $1.248 \mu\text{m}$  for the 20% HA-modified films. These changes indicate that the films now possess more pronounced surface features, enhancing potential interactions with their environment.

Surface modification with oligomers further amplified this effect. Improved HA–PLA compatibility promotes uniform particle dispersion, reduces agglomeration, and allows individual particles to act more effectively as roughness-enhancing agents. This is reflected in the increased Peak Density and Peak Area values in the modified films.

Overall, the addition and surface modification of HA significantly enhance the topography of PLA films, producing well-defined, functional surface features that can be advantageous for applications requiring enhanced surface interactions or functionalization.

**3.4 Contact angle:** The contact angle analysis, presented in and figure 5, reveals that the addition of hydroxyapatite (HA) and its surface modification have a complex and non-linear effect on the wettability of PLA. Contrary to the initial assumption that HA is inherently hydrophilic, the results show variable behavior.



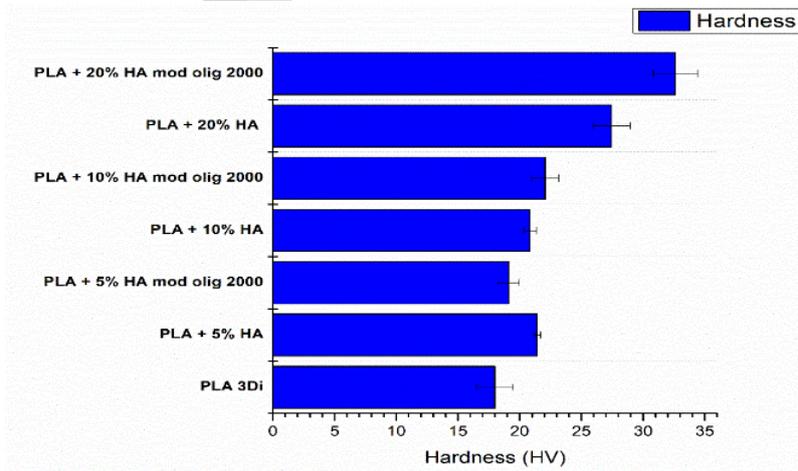
*Figure 5. Contact Angle Values of PLA Composites*

Pure PLA is hydrophobic (57°). Unmodified HA generally increased the contact angle (up to 77°), suggesting suboptimal dispersion that temporarily enhances hydrophobicity.

Crucially, the 20% HA film modified with PLA 2000 oligomers achieved the lowest contact angle (≈44°). This demonstrates that the combination of high filler concentration and effective surface modification is necessary to achieve optimal particle dispersion and a significantly more hydrophilic surface.

Wettability control requires optimizing both HA concentration and surface chemistry.

**3.5 Vickers hardness test:** The Vickers hardness test was conducted to evaluate the indentation resistance of the PLA composites with varying HA additions. The results, presented in Table 5, confirm the reinforcing effect of HA on the PLA matrix.

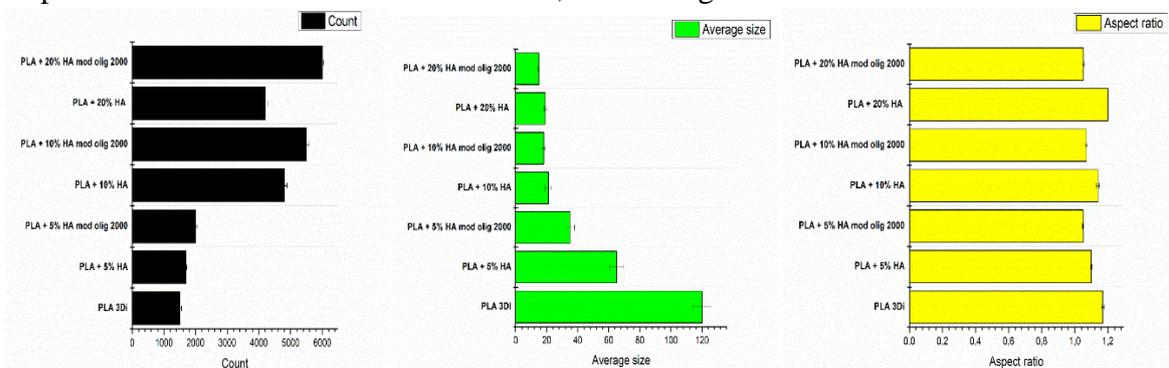


**Figure 6.** Vickers Hardness (HV) of PLA Composites

Unfilled PLA films exhibited a hardness of 17.97 HV. The incorporation of unmodified HA progressively increased hardness with concentration, reaching 21.4 HV, 22.05 HV, and 27.43 HV for 5%, 10%, and 20% HA, respectively. This enhancement is attributed to the intrinsic rigidity of HA, which acts as a ceramic reinforcement, restricting plastic deformation of the polymer matrix under applied load.

Films containing modified HA exhibited a more complex behavior. At lower concentrations (5% and 10%), hardness was slightly lower than that of the unmodified counterparts (19.1 HV and 20.8 HV), likely due to improved compatibility with the oligomer, which may reduce local interfacial stiffness while promoting better dispersion. In contrast, the 20% HA-modified films showed a substantial increase in hardness, reaching 32.6 HV—the highest value observed. This indicates that at high HA loading, surface modification optimizes particle dispersion and interfacial adhesion, enabling more effective load transfer and producing a more penetration-resistant material.

**3.6 Optical microscope (Zeiss):** Optical micrograph analysis was conducted to investigate the dispersion of hydroxyapatite (HA) particles in the poly(lactic acid) (PLA) matrix and to evaluate the effectiveness of the surface modification of HA with PLA oligomers. The results, presented in Table 6, reveal a clear and consistent improvement in dispersion across all concentrations studied, confirming the success of the surface treatment.



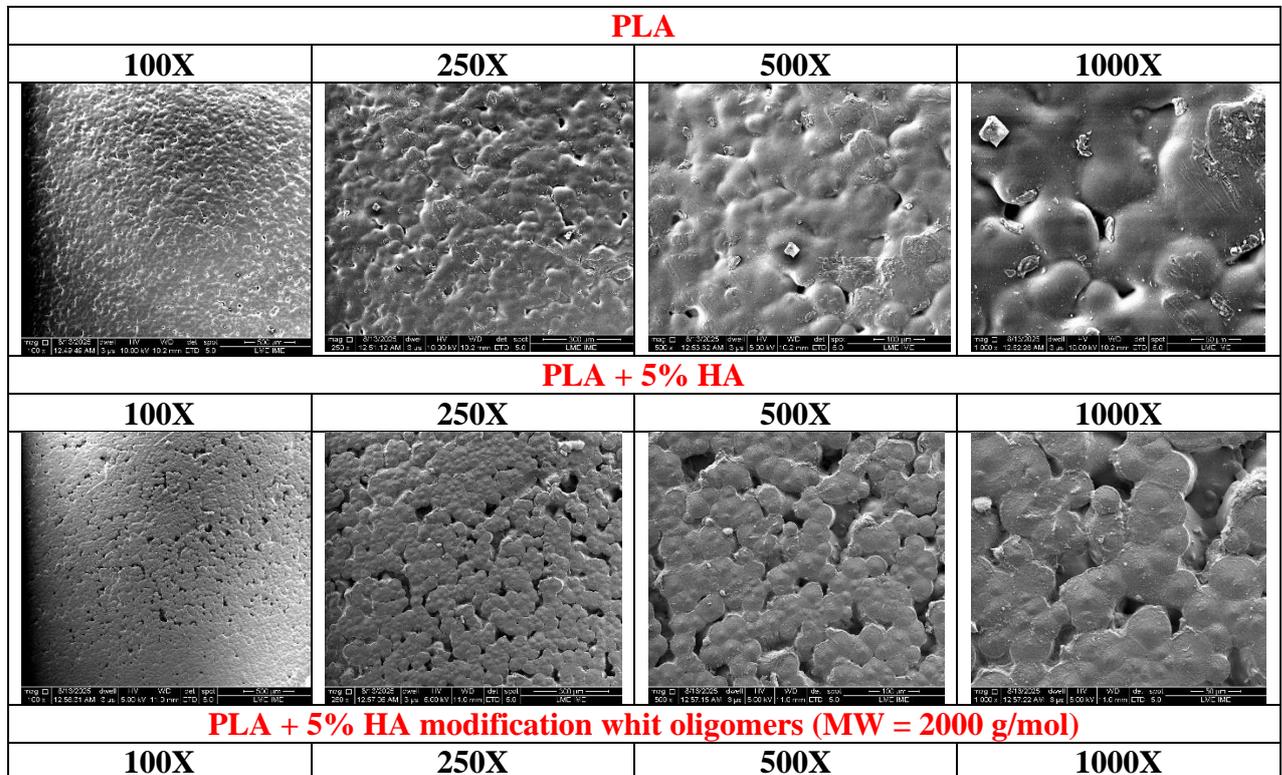
**Figure 7.** Optical Microscopy (Zeiss) grafics.

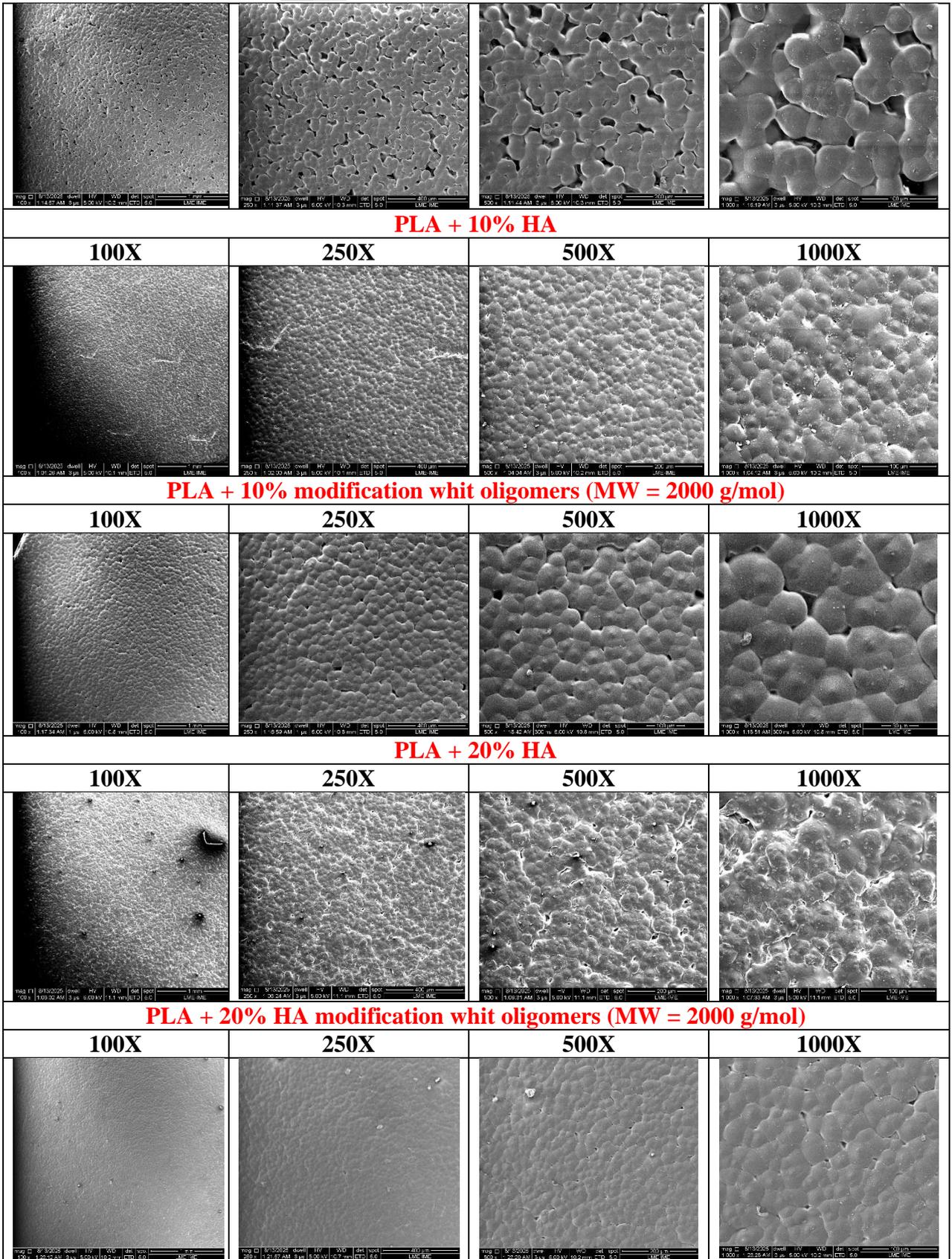
Optical microscopy at 10 X magnification was used to evaluate particle dispersion. The results clearly demonstrate that surface modification with PLA oligomers significantly enhanced HA compatibility with the PLA matrix, promoting more uniform dispersion and preventing agglomeration.

- **Increased Particle Count and Reduced Size:** Modification consistently increased the counted number of particles (indicating reduced agglomeration) and decreased the average particle size.
  - At 5% HA, the average size dropped significantly (from 65 $\mu$ m to 35 $\mu$ m) and the count increased (1,700 to 2,000).
  - The effect was most pronounced at 20% HA, where the particle count reached 6,000 and the average size dropped to 15 $\mu$ m, suggesting near-perfect distribution.
- **Aspect Ratio:** Modified samples consistently maintained a low aspect ratio (close to 1), confirming the formation of spherical, well-dispersed particles rather than the irregular, elongated agglomerates seen in unmodified samples.

This improved, homogeneous particle distribution is critical for establishing a robust matrix–reinforcement interface, which is essential for optimizing the overall mechanical and surface properties of the composites.

**3.7 Scanning Electron Microscopy (SEM):** The results from the scanning electron microscopy (SEM) provide a qualitative view of how different HA concentrations and modification with oligomers influence the morphology of the PLA material's surface. A detailed analysis of what can be observed in these micrographs is presented below.





Morphological observations were conducted using scanning electron microscopy (SEM) to evaluate the initial surface of the films, prior to any degradation or mechanical testing. Samples included neat PLA, PLA with unmodified hydroxyapatite (HA), and PLA with hydroxyapatite modified with PLA oligomers of molecular weight 2000 (HA-PLA<sub>2000</sub>), analyzed at 5, 10, and 20 wt%.

In the micrographs of unmodified HA samples, surface-visible particles were identified, some forming agglomerates, with interfacial regions showing less uniform adhesion to the polymer matrix. Conversely, films containing modified HA displayed a more homogeneous particle distribution, with reduced agglomeration and a more continuous interface between the organic and inorganic phases.

These observations indicate that surface modification of HA with PLA oligomers improves particle-matrix compatibility and wetting, reducing interfacial energy and promoting uniform dispersion throughout the matrix. The morphological differences provide clear evidence of the effectiveness of the surface treatment, which likely contributes to enhanced mechanical performance and stability of the composites.

#### 4 Discussion of Results

The present study successfully demonstrates that the incorporation of hydroxyapatite (HA) and its surface modification with PLA 2000 oligomers are critical parameters for tuning the mechanical, thermal, and surface characteristics of solvent-cast PLA films. Our findings are fundamentally governed by the modification's ability to engineer the polymer-ceramic interphase ((5),(6),(7)).

Morphological analysis revealed that the PLA 2000 shell acted as a molecular bridge, significantly enhancing the compatibility of HA with the hydrophobic PLA matrix. This was evidenced by a substantial improvement in particle dispersion, with modified HA exhibiting a higher effective count, smaller average size, and a low Aspect Ratio ( $\approx 1$ ) ((4), (8),(9)). Mechanistically, the coating partially screens the polar surface groups of HA, promoting the formation of "soft agglomerates" where the polymer shell interpenetrates the matrix, a prerequisite for efficient wetting (1), (2), (5)) and reducing the formation of microvoids that act as Griffith flaws (9).

This improved interfacial adhesion directly translated into superior mechanical performance. The Elastic Modulus and Vickers Hardness increased progressively with HA content, reaching maximum values for the 20% modified HA film ((1), (4), (8), (13)). This result is a direct testament to the enhanced load-transfer efficiency, consistent with micromechanical models where grafting increases the interfacial efficiency factor by shear-locking the inclusion to the matrix ((1), (4), (8)). While HA incorporation resulted in the expected tradeoff a decrease in Strain at Break ((1), (4), (8), (13)), the surface modification mitigated the reduction in Tensile Strength. By reducing the elastic mismatch and blunting defects through a tougher interphase, the modified HA particles delayed debonding and reduced stress localization compared to unmodified samples ((4), (8), (13)).

The thermal properties showed that the fundamental nature of PLA remained stable, with T<sub>g</sub> and T<sub>m</sub> being unaffected. However, Crystallinity was highly sensitive to concentration and modification. At low loadings 5%, the modified HA particles acted as highly effective heterogeneous nucleating sites, leading to the highest observed crystallinity (10). Conversely, at high concentrations 20%, the dense packing of the filler restricted polymer chain mobility, which suppressed crystal growth and negated the nucleating effect (10).

Finally, the improved dispersion critically dictated the surface properties. The 20% modified HA film exhibited a significant increase in surface roughness (Ra), coupled with a marked shift toward hydrophilicity (lowest contact angle of  $\approx 44^\circ$ ) ((11), (12)). This

enhanced wettability is a consequence of the optimal particle distribution, which maximizes the exposure of polar HA groups at the surface, aligning with the Wenzel regime for rough, hydrophilic surfaces ((11), (12)).

In conclusion, the PLA 2000 oligomer modification is essential for optimizing PLA–HA composite performance. While low HA content is ideal for maximizing crystallinity and preserving ductility, the use of modified HA at high concentrations ( $\approx 20\%$ ) is the most effective strategy for simultaneously maximizing stiffness, hardness, roughness, and surface hydrophilicity ((4), (8), (13)). These findings provide clear guidance for designing functional polymer-ceramic films for advanced applications.

## 5 Conclusions

1. Effect of HA Content: Incorporating HA into PLA films significantly alters their mechanical, thermal, and surface properties, with low HA levels enhancing crystallinity and ductility, and higher levels increasing stiffness, hardness, and hydrophilicity.
2. Role of Surface Modification: Surface modification of HA with PLA oligomers effectively improves particle dispersion, reduces agglomeration, and reinforces the polymer–ceramic interface, resulting in superior mechanical and surface performance.
3. Mechanical Trade-Off: Tensile testing revealed a stiffness–ductility trade-off; films containing modified HA achieved higher elastic modulus and hardness while only partially reducing tensile strength.
4. Thermal Behavior: DSC analysis showed that HA acts as a nucleating agent at low concentrations but restricts crystallization at high loadings due to limited polymer chain mobility, emphasizing the need to optimize HA content.
5. Surface Properties: Surface roughness and contact angle measurements confirmed that both HA incorporation and surface modification strongly affect topography and wettability, with high modified HA content producing the roughest and most hydrophilic surfaces.
6. Microstructural Evidence: Optical microscopy and SEM analyses supported the improved dispersion and enhanced interface quality in films containing modified HA.
7. Overall Implication: These findings demonstrate that adjusting HA concentration and surface chemistry provides an effective strategy to tailor the functional performance of PLA–HA composite films for advanced applications.

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