

Article

Chitosan Enhanced Polymers for Active Packaging: Intelligent Moisture Regulation and Non-Invasive Assessment

Jesús R. Villegas Méndez ¹, María Maura Téllez Rosas ¹, Rafael Aguirre Flores ², Felipe Avalos Belmontes ^{1,3},
Francisco J. González ^{1,*} and Mario Hoyos ^{4,*}

¹ Facultad de Ciencias Químicas, Universidad Autónoma de Coahuila, Blvd. Venustiano Carranza, S/N, República Oriente, Saltillo 25280, Coahuila, Mexico; jesus.villegas@uadec.edu.mx (J.R.V.M.); mauratellez@uadec.edu.mx (M.M.T.R.); favalos@uadec.edu.mx (F.A.B.)

² Procesos de Transformación de Plásticos, Centro de Investigación en Química Aplicada, Blvd, Enrique Reyna Hermosillo, 140, San José de los Cerritos, Saltillo 25294, Coahuila, Mexico; rafael.aguirre@ciqa.edu.mx

³ Universidad Tecnológica de Coahuila, Av. Industria Metalúrgica, Blvd. Del Parque Industrial Francisco R. Alanís 2001, Ramos Arizpe 25900, Coahuila, Mexico

⁴ Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), c/Juan de la Cierva, 3, 28006 Madrid, Spain

* Correspondence: fgonzalezgonzalez@uadec.edu.mx (F.J.G.); hoyos@ictp.csic.es (M.H.)

Abstract

This work presents the non-destructive assessment of polymeric composites based on synthetic matrices low-density polyethylene (LDPE) and polystyrene (PS) enhanced with chitosan (CS) biopolymer for use in active packaging systems for moisture control. Composites were prepared by incorporating CS at different contents (1, 3 and 5 phr) into LDPE and PS matrices. To evaluate the structural and thermal alterations induced by biopolymer loading, the materials were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The composites' water-regulating properties—specifically, moisture absorption, retention, diffusion, and water vapor transmission rate—were quantitatively tracked. Furthermore, the mechanical integrity of both dried and water-exposed systems was assessed via Shore D hardness testing. The results reveal a direct correlation between CS concentrations and enhanced hydrophilic behavior and water absorption, primarily attributed to the polar hydroxyl and amine groups within its molecular structure. The composites maintained adequate mechanical strength even after water exposure, confirming their structural stability for practical applications. This study demonstrates that the incorporation of CS into non-polar synthetic matrices significantly improves water affinity without requiring chemical compatibilizers, representing a cost-effective route to develop responsive packaging. The promise of these composites as responsive materials for real-time environmental interaction is highlighted by the successful non-destructive monitoring of their performance. This research establishes the feasibility and efficacy of non-destructive monitoring techniques in developing active packaging technologies, accelerating the progress of polymer-based systems with integrated and tunable moisture regulation capabilities.

Keywords: composite materials; intelligent packaging; moisture control; nondestructive evaluation



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1. Introduction

The global need to reduce food waste and extend the shelf life of perishable products has driven the development of active and intelligent packaging systems capable of interacting with their surrounding environment to maintain optimal conditions during storage and

distribution [1–3]. Controlling the relative humidity (RH) inside packaging is critical, as excessive levels can accelerate microbial growth or cause condensation, while insufficient humidity can lead to product dehydration and loss of sensory quality [4,5].

To overcome this challenge, various hygroscopic materials have been proposed to act as passive or active humidity regulators [6,7]. Among them, chitosan (CS) has gained attention due to its biodegradable nature, high affinity for water, and antimicrobial properties, making it an excellent candidate for use in packaging systems [8]. In recent studies, CS has been blended with different thermoplastics, such as polylactic acid (PLA), polycaprolactone (PCL), and polyethylene derivatives, and has been shown to significantly alter the water barrier properties of the resulting composites, improving their capacity for moisture regulation under various environmental conditions [9–11]. However, its incorporation into polymer matrices such as low-density polyethylene (LDPE) and polystyrene (PS) requires a detailed analysis of structural compatibility, impact on functional properties, and, most importantly, performance under simulated use conditions [12–14].

The trajectory of active packaging research increasingly favors integrated composite solutions that simultaneously address multiple degradation pathways, such as moisture fluctuations and microbial contamination. A compelling example of this approach is presented by Dai et al. (2025), who developed innovative food packaging films derived from bamboo shoot shell cellulose nanofibers combined with a cinnamaldehyde/CS emulsion. Their work successfully demonstrated the feasibility of creating multifunctional bio-based films that are simultaneously mechanically robust, water-stable, and chemically active against spoilage agents [15].

Beyond simple material addition, the effective design of advanced packaging often relies on optimizing the material's internal architecture, frequently at nanoscale. For instance, Zhang et al. (2025) recently demonstrated a highly effective approach by fabricating a poly (vinyl alcohol) (PVA)/lignocellulose/poly (butylene adipate-co-terephthalate) composite utilizing a “sandwich” structure. This design resulted in a robust material exhibiting excellent water resistance and anti-ultraviolet properties, focusing on reducing water permeability (a passive barrier function) for shelf-life extension [16]. Further extending the knowledge base on bio-based enhancements, Papapetros et al. (2025) systematically investigated the structure–property correlations of PVA nanocomposite films reinforced with cellulose-based nanoparticles. Their study elucidated how the nanoscale dispersion and interfacial interactions fundamentally govern the resulting mechanical, thermal, and, critically, the water vapor transmission performance of the films [17].

However, the majority of the aforementioned studies focus either on fully bio-based systems or on improving the passive barrier function. A distinct research gap remains in applying these objective shifts, from minimizing water permeation to maximizing active water sorption and buffering capacity. Our current work addresses the effects resulting from the addition of CS to non-polar matrices, utilizing CS hydrophilicity for tunable moisture regulation.

Most studies on functional polymeric composites employ destructive characterization techniques, which involve irreversible fragmentation or modification of the samples. This approach limits the ability to monitor the real-time behavior of the material during its application. For this reason, nondestructive evaluation emerges as an efficient alternative to characterize composite materials without compromising their integrity, especially in systems that are expected to respond dynamically to environmental stimulus [18–20].

This approach enables the exploration of how the incorporation of a functional agent influences system response without resorting to destructive testing, thereby contributing to the design of intelligent materials capable of autonomously and sustainably regulating moisture and eliminating the need for compatibilizers or destructive testing. Similar

strategies have been increasingly adopted in the field of polymer-based composites, where non-destructive methods are prioritized to ensure the preservation of sample integrity while capturing reliable information on structural, thermal, and functional properties.

For example, Piekarska et al. (2023) provided an extensive overview of chitin and CS modifications in polymer systems, highlighting their ability to enhance moisture-barrier properties while maintaining biodegradability and functionality, using characterization approaches that preserved sample integrity [21]. In another case, Ren et al. (2024) demonstrated that the incorporation of nanocellulose into PVA films improved both thermal and barrier performance, with water vapor transmission rates evaluated by non-destructive methodologies such as gravimetric sorption and spectroscopy [22]. Complementary evidence comes from dynamic vapor sorption analyses applied to nanocellulose systems, where the sorption–desorption kinetics of water molecules were monitored without altering sample structure, confirming the relevance of such techniques for hygroscopic materials [23]. More recently, biopolymer films based on CS and pectin were characterized under non-destructive protocols, showing strong antimicrobial functionality combined with controlled water vapor transmission, reinforcing their potential in active food packaging [24].

These examples collectively emphasize the relevance of applying non-destructive methods to correlate methodology, results, and performance in humidity-regulating materials. By enabling the simultaneous assessment of thermal stability, crystallinity, moisture absorption, diffusion, and surface hardness without damaging the samples, these approaches offer a holistic understanding of material behavior. Furthermore, they bridge laboratory-scale evaluations with real-life functional requirements, where long-term stability, mechanical reliability, and controlled humidity regulation are essential.

In this work, the thermal, structural, hygroscopic, and mechanical properties of CS-functionalized LDPE and PS-based composites at concentrations of 1, 3 and 5 phr were evaluated. Techniques such as scanning electron microscopy (SEM), X-ray Diffraction (XRD), and differential scanning calorimetry (DSC) were used to assess the structural and thermal compatibility of the systems. Moisture absorption, retention, diffusion, and water vapor transmission (WVT) tests were conducted to monitor the functional behavior of the material under controlled environmental conditions. In addition, Shore D hardness was measured before and after exposure to humidity as an indirect indicator of structural integrity.

2. Materials and Methods

The raw materials for the composite preparation included two commercially sourced polymer matrices, LDPE and PS, with industrial grade purity in pellet form. LDPE has a melt flow index (MFI) of $15 \text{ g } 10 \text{ min}^{-1}$ (determined at 190°C with a 2.16 kg load) and a density of 0.92 g cm^{-3} . The PS exhibited an MFI of $5 \text{ g } 10 \text{ min}^{-1}$ (determined at 200°C with a 5 kg load) and a density of 1.04 g cm^{-3} . MFI values were obtained in accordance with the American Standard for Testing and Materials (ASTM) D1238 standard [25]. CS with crustacean origin and industrial grade purity was supplied in powder, with an average particle size of $75 \mu\text{m}$, molecular weight of approximately 500 kDa and a degree of deacetylation of 85%.

The blends were prepared by melt processing using a Rheocord System 40 internal mixer from Haake Buchler Instruments, Inc. (Paramus, NJ, USA). The equipment operated at a speed of 50 rpm for 10 min, maintaining a constant temperature of 160°C . In this study, eight formulations were prepared and analyzed to evaluate the effect of CS addition on the functional and structural properties of two different polymer matrices: LDPE and PS. A control sample consists of 100 phr of each polymer without additives, and composites incorporating CS at concentrations of 1, 3, and 5 phr, labeled as 1CSLDPE, 3CSLDPE, and 5CSLDPE for LDPE and 1CSPS, 3CSPS, and 5CSPS for PS.

Following film preparation, the visual appearance of the pure polymer films and the resulting composites was recorded to assess the macrostructural impact of the incorporated biopolymer. Figure 1 illustrates the visual aspect of the neat LDPE and PS films alongside their corresponding CS-composite (1, 3 and 5 phr). The pure LDPE and PS films exhibited their characteristic white/translucent appearance. In contrast, all composites showed a clear color transition towards a yellowish-brown hue, with the intensity of the color directly correlating with the increasing concentration of CS filler. This noticeable change in color and transparency confirms successful physical incorporation of the biopolymer into both non-polar LDPE and PS matrices. The observed darkening is primarily attributed to the inherent CS powder color. These macroscopic observations require a deeper analysis, which was subsequently performed using microstructural analysis as SEM to evaluate internal morphological alterations induced by the CS loading in the synthetic polymers.

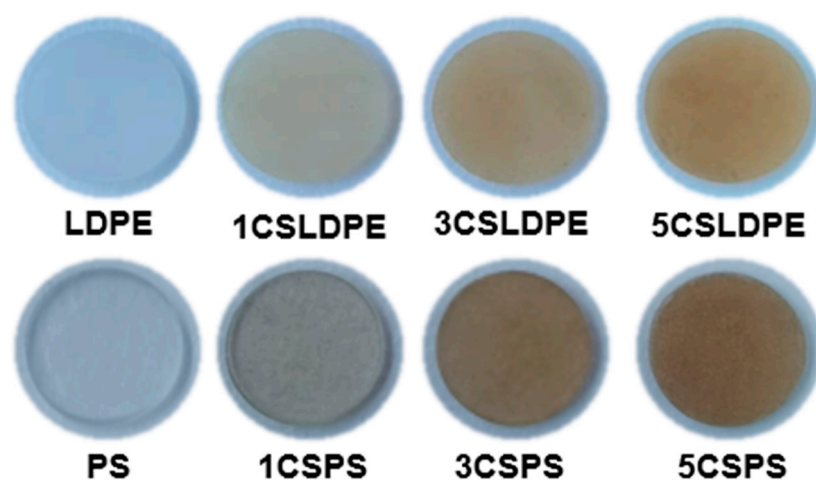


Figure 1. Visual appearance of pure polymer films and their CS composites.

First, the thermal stability of the individual raw materials was evaluated by thermogravimetric analysis (TGA) using a Perkin Elmer TGA 4000 (Perkin Elmer Co., Shelton, CT, USA). The measurements were conducted under an inert nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, ranging from $30\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$. However, it is important to note that TGA, although inherently destructive, was employed in this study with the specific purpose of verifying the thermal degradation profiles of the raw materials. This step ensured that subsequent thermal analyses would not expose the polymers to degradation temperatures.

Subsequently, to evaluate the morphology of the CS and its dispersion within LDPE and PS matrices, SEM analysis was performed using a JEOL JSM-6510 LV microscope (JEOL Co., Tokyo, Japan). The solid samples were previously sputtered with a thin layer of 99.99% pure gold to make the surface conductive. The crystalline phases in the composites were identified by XRD using an Empyrean Diffractometer (Malvern Panalytical Ins. Co., Malvern, UK), operating with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. The scan covered 2θ angles from 10° to 80° , with a scan rate of $0.026^{\circ}\text{ s}^{-1}$. The resulting diffractograms were compared with entries from the International Centre for Diffraction Data (ICDD) database to identify potential secondary phases [26].

Regarding the thermal behavior of the composites, glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and melting and crystallization enthalpies (ΔH_m and ΔH_c , respectively) were determined using a Perkin Elmer Diamond DSC, operating in a temperature range from $30\text{ }^{\circ}\text{C}$ to $160\text{ }^{\circ}\text{C}$, with a heating rate of

10 °C min^{−1}, under a nitrogen atmosphere. Additionally, the degree of crystallinity (χ_c) of the LDPE-based composites was determined using the following equation:

$$\chi_c = \Delta H_m \cdot \Delta H_{100}^{-1} \cdot 100 \quad (1)$$

where χ_c is the degree of crystallinity and ΔH_{100} is the melting enthalpy of 100% crystalline polyethylene, which is equal to 293 J g^{−1} [27].

To evaluate the functional properties related to water interaction, a comprehensive water barrier analysis of the composite materials was carried out. This analysis included the determination of moisture absorption, diffusion coefficient, WVT, mass loss due to soluble components, and surface hardness. Tests were conducted under controlled RH conditions ranging from 40% to 100%, simulating different storage environments.

The measurements of absorption percentage (%Abs), water diffusion coefficient (D), and soluble matter loss (%SML) were performed in accordance with ASTM D570 [28]. The %Abs was calculated using the following equation:

$$\%Abs = (WW - DW) \cdot DW^{-1} \quad (2)$$

where WW is the wet weight and DW is the dry weight of the sample.

In contrast, the %SML was calculated according to the following expression:

$$\%SML = (IW - DW) \cdot IW^{-1} \quad (3)$$

where IW is the initial weight of the sample.

To determine the D, equations derived from the Fickian diffusion model adjusted by Almudaihesh et al. (2022) were utilized. Specifically, the uncorrected water diffusion coefficient (D_0) was calculated as follows [29]:

$$D_0 = \pi \cdot \left[h \cdot \left(4 \cdot \left(\%M_f \right) \right) \right]^{-2} \cdot \left[(\%M_2 - \%M_1) \cdot (\sqrt{t_2} - \sqrt{t_1}) \right]^{-2} \quad (4)$$

where h is the specimen thickness, $\%M_f$ is the maximum absorption percentage, and $\%M_1$ and $\%M_2$ are the absorption percentages at times t_1 and t_2 , respectively, corresponding to the beginning and end of the Fickian absorption slope. To account for edges effects related to specimen geometry, the following corrected expression was applied:

$$D = D_0 \cdot [1 + h/l + h/w]^{-2} \quad (5)$$

Here, l and w represent the length and width of the sample, respectively. For circular specimens, these values corresponded to the sample radius. This correction provided a more accurate value for the diffusion coefficient by accounting for three-dimensional moisture migration.

In addition, WVT values were determined using the procedures described in ASTM E96 [30], applying the following expressions:

$$WVT = WG \cdot t^{-1} \cdot A^{-1} \quad (6)$$

where WG is the weight gain between two points on the water transmission curve, t is the time interval corresponding to that gain and A is the specimen area.

Surface hardness was measured according to ASTM D2240 [31] using a Shore D durometer with a range of 0–100 hardness (HD) and a precision of 0.5 HD. All tests were performed in triplicate for each formulation, and the results are reported along with their

corresponding standard deviations. Table 1 lists all the analyses and methods used and their parameters or standards.

Table 1. Analyses and methods used during this research.

Technique/Method	Parameters/Standard
TGA	Heating rate of 10 °C min ^{−1} , ranging from 30 °C to 600 °C.
XRD	CuK α radiation at 40 kilovolts (kV) and 30 milliamperes (mA). The scan range covered 2 θ angles from 10° to 80°, with a scan rate of 0.026° s ^{−1} .
DSC	Temperature ranges from 30 °C to 160 °C, with a heating rate of 10 °C min ^{−1} , under a nitrogen atmosphere
Water absorption/diffusion	ASTM D570
WVT	ASTM E96
Hardness	ASTM D2240

3. Results and Discussion

3.1. Determination of Raw Material Thermal Stability

Figure 2 shows the TGA analysis of the raw materials, where the mass of the components is observed as a function of temperature. The onset temperature (T_{onset}) of each component was identified, with LDPE, PS, and CS around 382.50 °C, 327.50 °C, and 253.78 °C, respectively. These T_{onset} values are consistent with values reported by other authors using similar materials [32,33]. Additionally, an initial mass loss attributed to water evaporation from CS was observed around 100 °C. Based on these results, a processing temperature (T_p) of 160 °C was selected as appropriate for fabricating the composites.

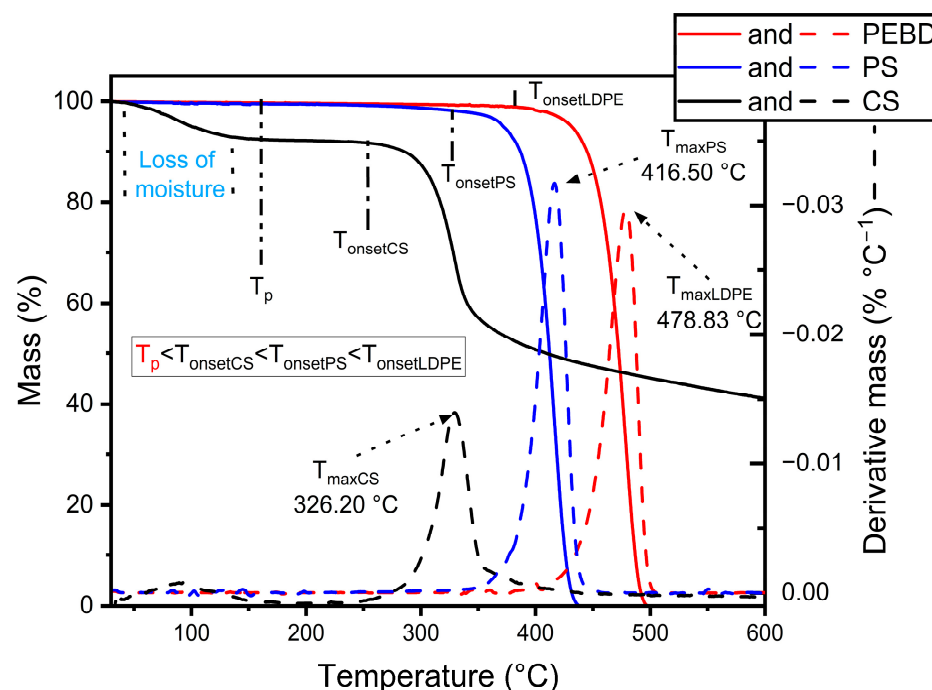


Figure 2. TGA curves of the raw materials' thermal stability.

Figures S1 and S2 present the TGA curves for pure LDPE, PS and their composites. The data highlights the CS-induced reduction in the T_{onset} and the T_{max} of the LDPE and PS matrix, confirming a slight decrease in thermal stability proportional to the CS loading. The residual water content was calculated for each material with values of 0%, 0.11%, 0.3%

and 0.35% for the LDPE, 1CSLDPE, 3CSLDPE and 5CSLDPE, respectively; in the same way, the values for PS, 1CSPS, 3CSPS and 5CSPS were 0.05%, 0.24%, 0.32% and 0.40%.

3.2. Morphological Analysis

Figure 3 illustrates the SEM results, beginning with the morphology of the raw CS (Figure 3a), which reveals angular and irregular shaped particles with a broad size distribution, ranging approximately from 20 to 100 μm . These features are consistent with unprocessed CS powders reported in the literature, which often have non-spherical geometry and high surface roughness due to their biogenic origin [34].

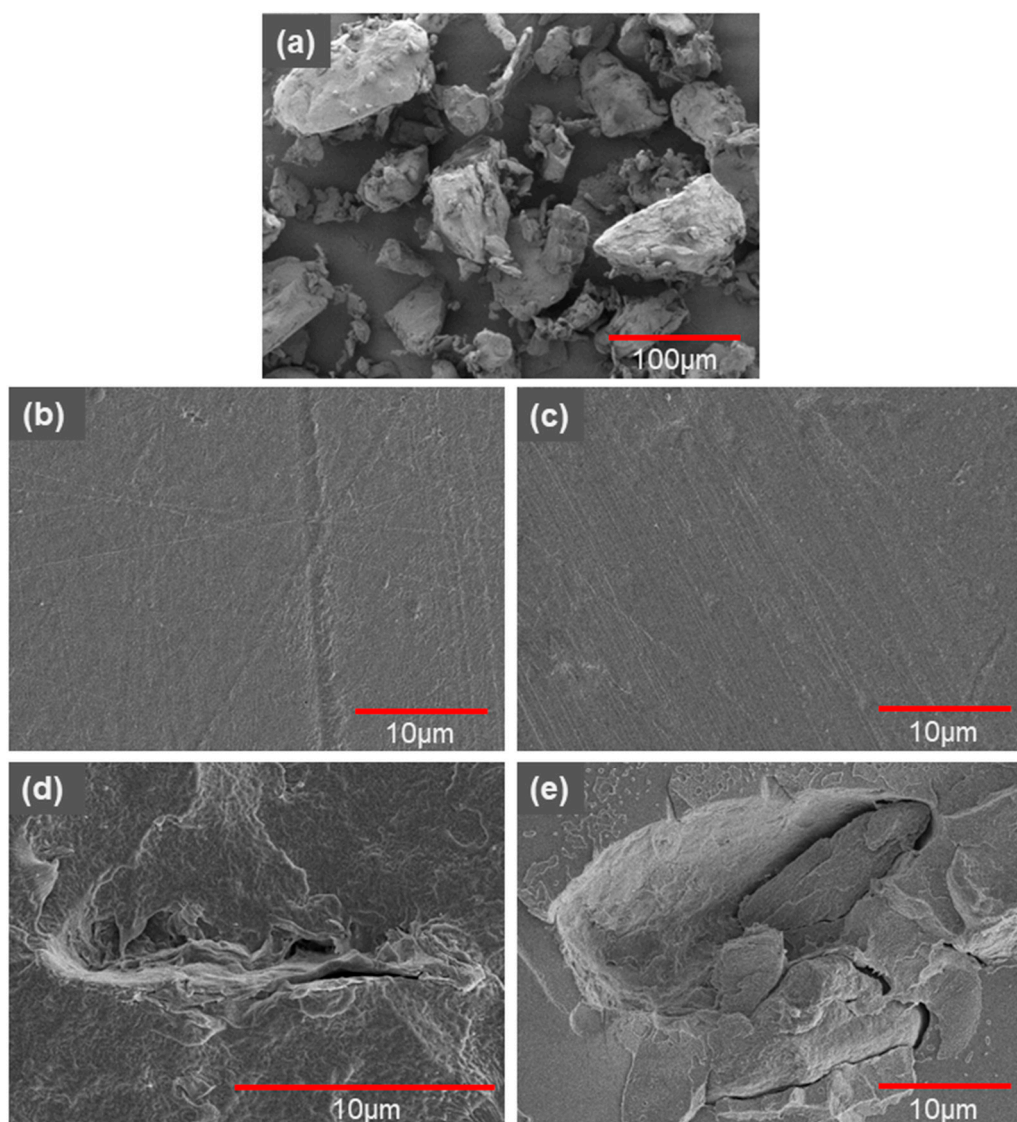


Figure 3. SEM images of (a) CS; (b) LDPE; (c) PS; (d) 5CSLDPE; and (e) 5CSPS.

The neat polymer matrices show markedly different microstructures. In the case of LDPE (Figure 3b), a homogeneous and smooth surface is observed, characteristic of semicrystalline thermoplastics processed under controlled thermal conditions. Similarly, the PS matrix (Figure 3c) shows a dense and uniform fracture surface with no visible inclusions or microstructural discontinuities, in agreement with its amorphous nature and brittle fracture behavior [35].

Upon incorporation of 5 phr of CS, clear morphological changes are detected, primarily indicative of poor interfacial compatibility between the highly polar CS and the non-polar

polymer matrices. In 5CSLDPE composite (Figure 3d), the presence of embedded CS particles is evident. A notable feature is the gap or void observed at the interface between the CS and the polymer with limited interfacial adhesion, a phenomenon previously reported for CS-polyolefin systems without compatibilizers [36]. In the 5CSPS (Figure 3e), the CS particles are also distinguishable, showing a more defined spherical contour in some cases and appearing more superficially localized. The presence of fractured particles and clear demarcation lines around the filler further corroborates the phase separation. The difference in dispersion patterns between LDPE and PS composites—where PS appears to restrict effective particle distribution—may be attributed to the higher viscosity and reduced mobility of the amorphous PS during processing.

3.3. Crystal Phases Determination

The XRD patterns of the composites revealed the characteristic signals of each polymeric matrix (Figure 4a,b). In the case of LDPE, the diffraction peaks associated with the crystalline phase around 21.6° and 23.9° remained present in all formulations [37]. In contrast, the PS patterns (an amorphous material) did not show significant changes in PS's broad peak around 20° [38], indicating that the incorporation of CS does not induce major reorganization of the matrix. No new peaks were observed in any of the formulations that would suggest the formation of distinct crystalline phases or severe phase incompatibility, which supports the partial integration of CS into both matrices [39].

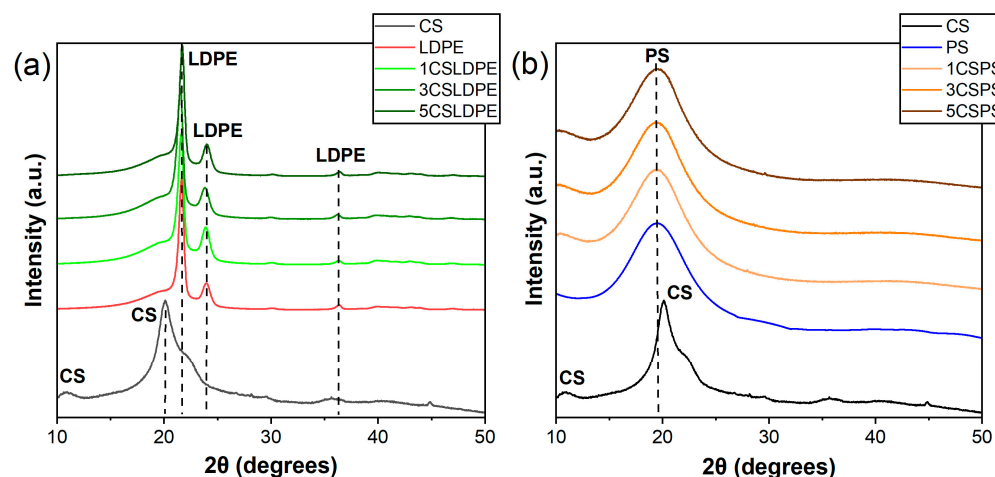


Figure 4. Diffractograms of (a) LDPE and (b) PS composites.

3.4. Thermal Analysis

To address the potential influence of moisture, all samples were subjected to a rigorous drying protocol prior to analysis. The DSC first curves (Figures S4 and S5) confirmed the successful elimination of free water, evidenced by the absence of significant endothermic events below 100°C (LDPE) and the constancy of PS T_g , indicating that residual moisture did induce a plasticizing effect on the polymer matrices. The DSC curves (Figure 5a,b) showed that the ΔH_m of LDPE decreased by approximately 5% when 3 phr of CS were added, followed by a partial recovery at 5 phr of CS (Table 2). This behavior suggests a partial disruption and reorganization of the crystalline domains in the presence of the biopolymer. The reduction in ΔH_m at intermediate concentrations indicates a corresponding reduction in the overall χ_c . Similar reductions in the crystalline with low CS content have also been reported by Agnes et al. (2024). The T_m of LDPE remained constant despite the incorporation of CS ($\sim 113^\circ\text{C}$), while the T_c exhibited a slight decrease ($\sim 1\text{--}2^\circ\text{C}$) upon CS addition (Table 2). This indicates that the crystallization kinetics may be affected by the presence of interfacial regions that promote nucleation of the polymer chains [40,41].

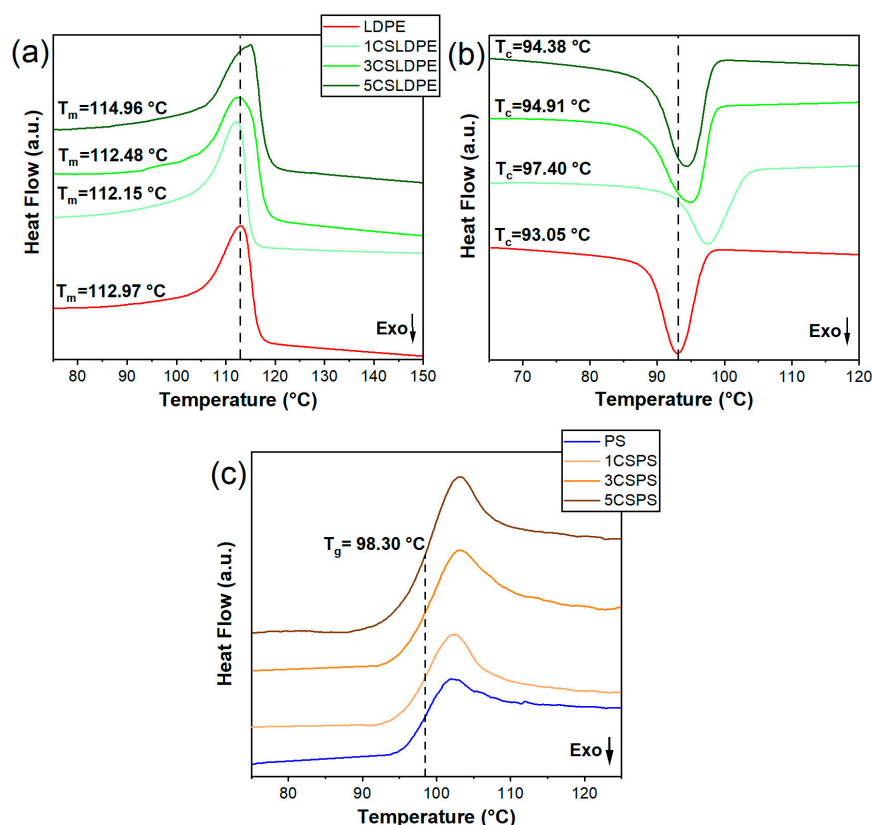


Figure 5. DSC curves: (a) LDPE composites during the melting process; (b) LDPE composites during the crystallization process; and (c) PS composites during the glass transition.

Table 2. Melting and crystallization temperatures, enthalpies and crystallinity degree.

	T_m	ΔH_m	T_c	H_c	χ_c
Composite	(°C)	(J g ^{−1})	(°C)	(J g ^{−1})	
LDPE	113.3	45	93	67.6	15.3
1CSLDPE	112.1	42.3	97.4	65.4	14.4
3CSLDPE	112.4	40.1	94.9	64.3	13.6
5CSLDPE	115.1	45.7	94.3	62.6	15.6

On the other hand, the constant T_g of PS (Figure 5c), around 98.3 °C, without significant changes suggests that CS does not interfere with the T_g . This lack of T_g variation suggests that there is no significant physical interaction or strong molecular bonding between the non-polar PS chains and the polar CS biopolymer. This observation aligns with previous studies indicating that the incorporation of biopolymeric fillers into amorphous matrices often does not induce major changes in chain mobility unless specific chemical compatibilizers are used or the filler content is higher than the shown in this study. This confirms that the observed functional changes in the PS/CS composites are primarily governed by the physical presence and distribution of the CS filler rather than by strong polymer–filler interactions [42,43].

While the thermal behavior of the pure polymer matrices was clearly defined, the DSC analysis of pure CS confirmed the complexity frequently reported in the literature. Figure S3 presents the DSC curves of CS during the first and second cycles, which reinforces the difficulty in assigning a specific T_g for CS and justifies focusing the mechanistic discussion on the LDPE and PS matrix transitions [44].

3.5. Water Barrier Properties

Figure 6 shows the behavior of soluble matter loss in the different composites as the HR increases from 40% to 100%. The general trend indicated that formulations with higher CS content tend to exhibit higher water retention, particularly under high HR ($\geq 95\%$).

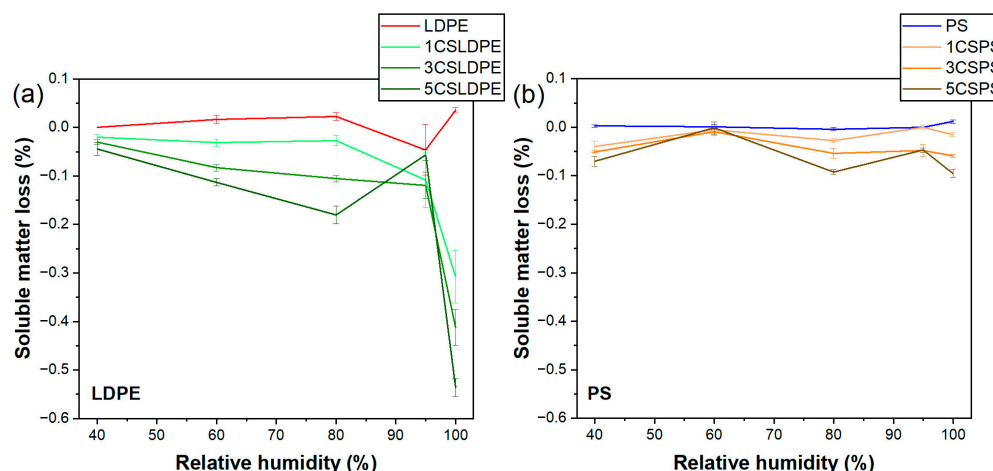


Figure 6. Graphs of the composites' soluble matter loss: (a) LDPE and (b) PS composites.

The 5CSLDPE system presents the most pronounced retention, reaching values close to -0.55% at 100% RH, followed by 3CSLDPE and 1CSLDPE in decreasing order (Figure 6a). This behavior is primarily due to the CS biopolymer reaching its maximum hygroscopic capacity near saturation. At high RH, the CS component absorbs large amount of water, causing localized swelling and facilitating maximum moisture uptake through potential hydrophilic pathways in the LDPE matrix. Conversely, the significant upturn in mass gain observed in the neat LDPE film around 95% RH is characteristic of the surface absorption and potential micro-capillary condensation of water molecules, which becomes pronounced when the atmosphere is becoming saturated, marking a shift from bulk vapor diffusion to surface-dominated interaction [45].

In contrast, PS-based composites (pure PS and CSPS) show lower water retention within their internal structure (Figure 6b). Both the pure PS and the 1CSPS system exhibit virtually no retention, remaining close to 0% even at elevated RH. However, as the CS content increases, the 3CSPS and 5CSPS systems show a slight mass gain (~ 0.1 – 0.2%), although still significantly lower than their LDPE counterparts. This suggests that the PS matrix offers a more permeable barrier due to its amorphous structure [46].

An interesting feature is that in both LDPE and PS systems, mass loss remains relatively stable up to 80–90% RH and undergoes a sudden shift only at 100%. This discontinuity suggests the presence of a water saturation threshold within the system, beyond which a microstructural disorganization of the embedded biopolymer occurs, causing it to retain moisture in its network that would require higher temperatures for evaporation [47].

Figure 7 presents the water uptake behavior of the pure polymer films and their composites over time under various RH conditions. The LDPE/CS composites consistently exhibit an increase in water absorption capacity and absorption rate proportional to both the applied RH and the CS loading. For pure LDPE, the water uptake remains minimal, reaching a value near to 0.05% after 200 h across all humidity levels (Figure 7a,b).

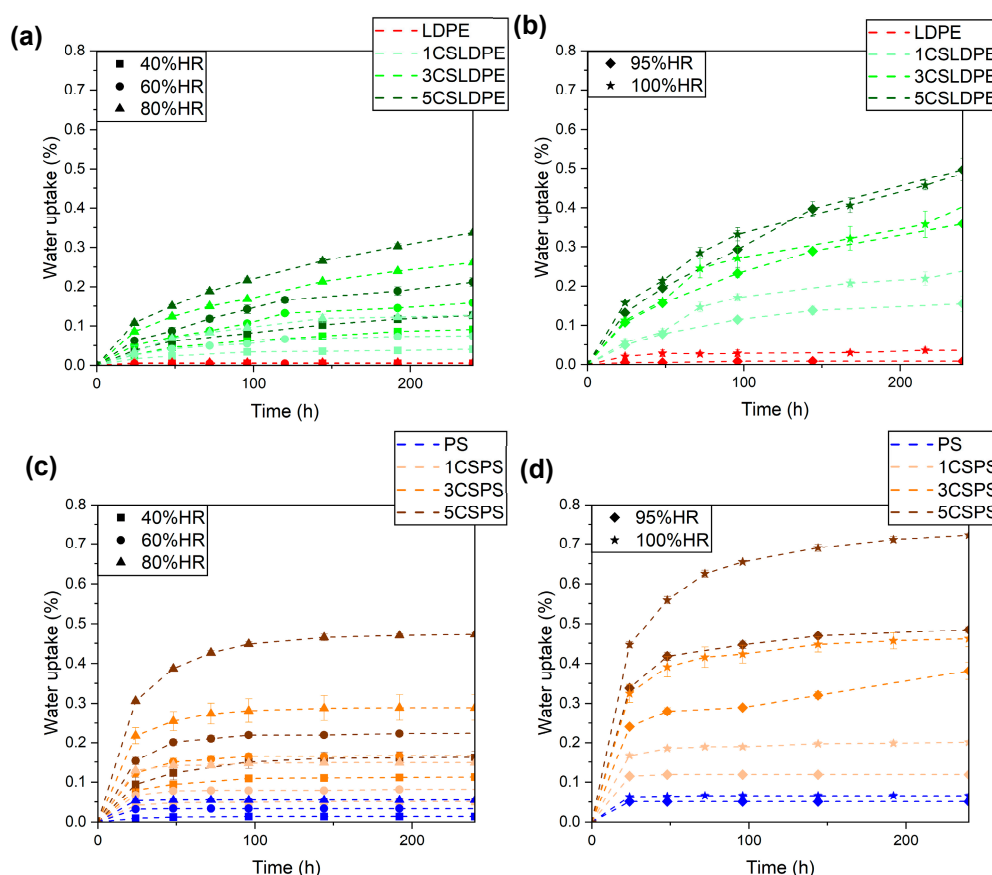


Figure 7. Water absorption graphs: (a,b) LDPE and (c,d) PS composites.

In contrast, the CS-enhanced LDPE composites show a progressive increase. The 5CSLDPE formulation significantly enhances the material's interaction with moisture, reaching values around 0.22% after 200 h at 95% RH (Figure 7b). This represents a nearly four-fold increase compared to the neat LDPE film, strongly indicating that the addition of CS effectively introduces active moisture-buffering capabilities, which is a desirable feature in active packaging applications [48].

The PS/CS systems demonstrate a remarkably greater moisture affinity. The curves for all PS/CS composites show faster kinetics and a higher equilibrium water content compared to their LDPE counterparts, especially at high CS concentrations (Figure 7c,d). The 5CSPS system stands out as the material with the highest absorption across all tested humidity levels. It reaches values above 0.7% after 200 h at 100% RH (Figure 7d).

This suggests that, although PS is inherently hydrophobic, the increasing CS content leads to the formation of a more continuous or accessible network of hydrophilic regions. This network significantly enhances moisture uptake, even within the amorphous PS matrix, potentially through the formation of CS-rich vesicles that modify water diffusion [49]. The faster absorption rate observed for PS composites also points to a more efficient diffusion mechanism compared to LDPE systems.

A consistent and critical pattern in both matrices is the acceleration of the absorption rate and the more pronounced increase in the equilibrium water uptake when the RH shifts from the intermediate range (e.g., 60% to 80% RH) to high saturation levels (e.g., 95% to 100% RH).

This behavior is indicative of a change in the moisture retention mechanism at high humidity. Within this range, the high concentration of water vapor promotes stronger hydrogen bonding between water molecules and the highly polar amino ($-NH_2$) and hydroxyl ($-OH$) groups of the CS biopolymer [50]. This suggests that multilayer absorption and cap-

illary condensation become the dominant factors at saturation, leading to increased water mobility inside the material and a corresponding jump in the overall absorption capacity.

The superior absorption capacity of the PS-based composites, compared to the LDPE counterparts at the same CS concentration, can be fundamentally explained by the nature of the polymer matrix. As an amorphous polymer, PS possesses a longer intrinsic free volume and allows for greater internal chain mobility than the semi-crystalline LDPE. This larger free volume facilitates both faster water diffusion and the formation/expansion of the CS-rich regions, thereby maximizing the hygroscopic potential of the added biopolymer [51].

Figure 8, which corresponds to the diffusion coefficient, displays the behavior of the composite materials as a function of RH. In general, unmodified LDPE exhibits the highest diffusion values across almost the entire RH range studied, with coefficients on the order of $1.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. This behavior is attributed to the semicrystalline structure of LDPE, which facilitates more defined transport channels for water vapor migration in the absence of interface from functional additives. This result aligns with literature reports indicating that LDPE films without fillers present relatively high permeability due to the combination of crystalline and amorphous regions that allow for a certain degree of molecular mobility [52,53]. The balance between these two phases allows partial mobility of water vapor molecules through the amorphous matrix, leading to measurable permeability even in neat LDPE. Recent studies have confirmed that the proportion and distribution of crystalline lamellae versus amorphous interlamellar regions strongly influence diffusion kinetics and overall barrier performance. For instance, studies have shown that water vapor transmission decreases linearly in polymers with increasing crystallinity, consistent with the tortuous path model, where crystalline domains present diffusion barriers and higher chain mobility in amorphous regions [54,55].

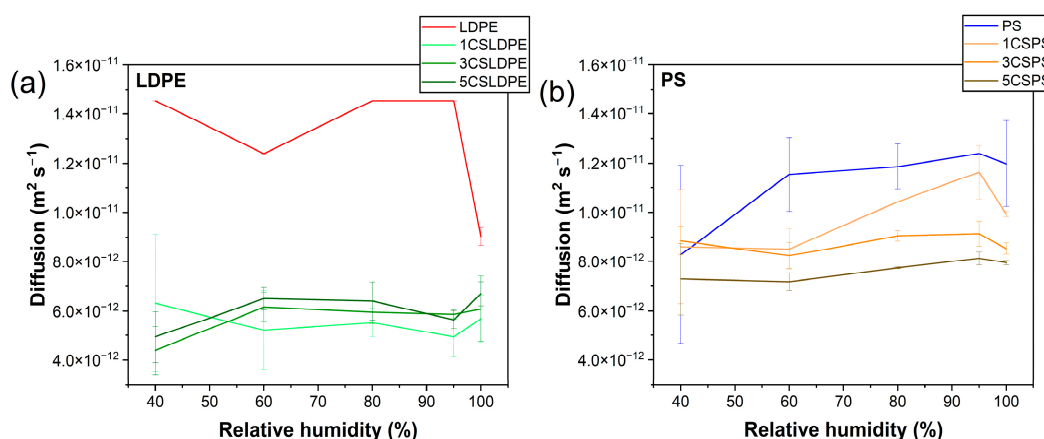


Figure 8. Relation between diffusion coefficients and relative humidity for (a) LDPE and (b) PS composites.

However, when CS is incorporated into the LDPE matrix, a progressive decrease in the diffusion coefficient is observed. The formulations containing 1, 3 and 5 phr of CS, exhibit significantly lower coefficients particularly in the case of 3CSLDPE and 5CSLDPE, whose values fall within the range of $4.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ to $6.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. This reduction can be interpreted because of the partial blockage of the internal transport pathways due to the presence of the biopolymer that increases the tortuosity [56]. Because of its hygroscopic nature, CS tends to retain moisture in localized regions, which limits the free flow of vapor through the polymer network of the LDPE [57]. Furthermore, its incorporation may introduce morphological heterogeneities (Figure 3) that increase resistance to water on both sides' interconnection, thus acting as an additional diffusion barrier [58].

In contrast, materials prepared from PS exhibit somewhat different behavior. Pure PS reaches diffusion values like those of LDPE, around $1.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, although with greater variability depending on the RH level. This variability is associated with the amorphous structure of PS, which offers more free volume, allowing for a more dynamic reorganization of the system in response to environmental changes [59]. When CS is incorporated into the PS matrix, a slight decrease in the diffusion coefficient is observed; however, the 1CSPS, 3CSPS, and 5CSPS formulations generally maintain relatively high values, ranging from $6.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ to $9.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. This suggests that, unlike LDPE, the incorporation of CS in PS does not drastically reduce diffusion, likely because the biopolymer is more efficiently redistributed within the amorphous matrix, without completely blocking vapor migration pathways.

Figure 9 shows a general WVT upward trend as the RH increases. This behavior is consistent with a greater vapor pressure gradient established between the environment and the interior of the material under high-humidity conditions. However, the magnitude and slope of the WVT growth vary significantly among the different composites.

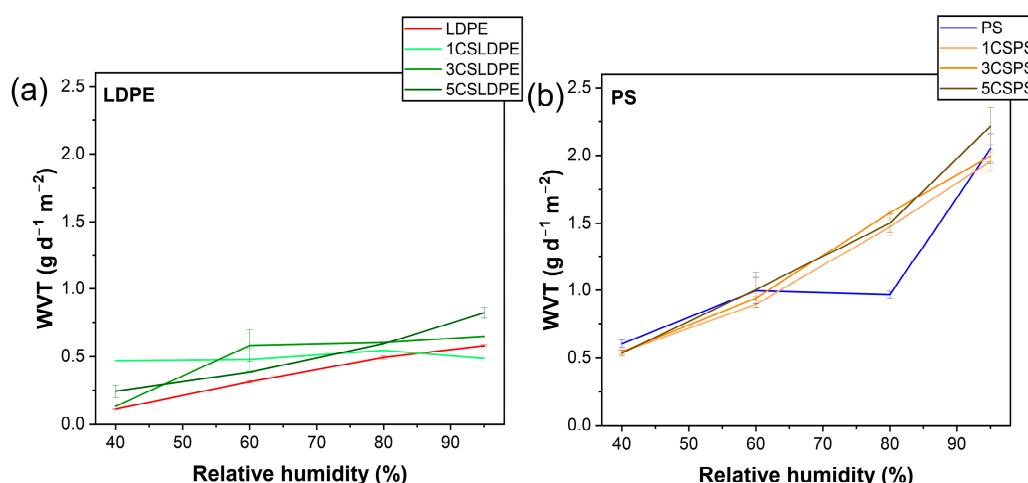


Figure 9. WVT values: (a) LDPE and (b) PS composites.

Pure LDPE exhibits the lowest WVT values, starting around $0.2 \text{ g d}^{-1} \text{ m}^{-2}$ at 40% RH and gradually increasing to approximately $0.6 \text{ g d}^{-1} \text{ m}^{-2}$ at 100%. This indicates that LDPE functions as an effective barrier against water vapor, which can be advantageous in applications where strict moisture control is required [60]. Nevertheless, the incorporation of CS into LDPE slightly increases the WVT. The 1CSLDPE and 3CSLDPE formulations show moderate increases compared to the neat matrix, while 5CSLDPE reaches higher values, suggesting that the CS phase introduces regions with greater water affinity, allowing free migration of vapor through the material [61].

On the other hand, PS-based formulations exhibit considerably higher vapor transmission rates. Pure PS, which begins with values around $0.6\text{--}0.7 \text{ g d}^{-1} \text{ m}^{-2}$, shows a marked increase as RH rises, reaching approximately $2.0 \text{ g d}^{-1} \text{ m}^{-2}$ at 100% RH. The 1CSPS, 3CSPS, and especially 5CSPS formulations follow a similar trend, with even slightly higher values. In the case of 5CSPS, the WVT surpasses $2.3 \text{ g d}^{-1} \text{ m}^{-2}$, suggesting that this system allows highly efficient vapor transmission, possibly due to the formation of a continuous network of hydrophilic microchannels induced by the CS [62].

This behavior can be explained by the interaction between CS and the PS matrix, since PS has an amorphous structure with larger free volume, CS may migrate toward the surface or distribute into interconnected domains that facilitate vapor passage. As environmental humidity increases, the system's ability to absorb and transport moisture also improves, producing a more pronounced functional response [63].

Overall, the results from both graphs allow for the definition of distinct functional profiles for each system. CS-modified LDPE acts as a passive barrier with a delayed response to humidity, suitable for products requiring slow release or extended protection against water vapor. In contrast, PS-based composites—particularly those with high CS content—exhibit a more dynamic behavior, with higher humidity transmission and a faster response to changes in RH. This type of material could be more suitable in applications where moisture buildup or internal condensation is expected, as it could efficiently regulate water content without compromising the structural integrity of the package [64].

3.6. Hardness Evaluation

Figure 10 shows how the Shore D hardness of the composites varies non-linearly with RH. In the case of raw LDPE, a notable decrease is observed as RH increases from 40% to 60% with values dropping from approximately 49 to 46 units. This trend reflects the plasticizing effect of moisture on the surface of the semicrystalline polymer, like what has been reported in CS-based systems, where increasing humidity leads to a reduction in the modulus and surface strength [65,66].

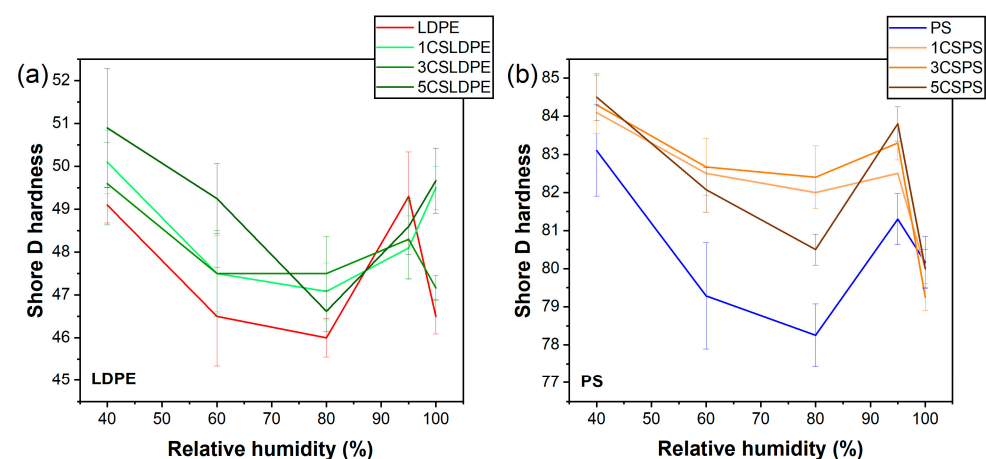


Figure 10. Shore D values for (a) LDPE and (b) PS composites.

When CS is incorporated into LDPE, the response changes; all LDPE composite systems exhibit higher hardness values at low RH, around 50–51 units. This suggests that the biopolymer slightly reinforces the material's surface structure. However, the decrease in hardness with increasing humidity is less pronounced in 3CSLDPE and 5LDPE compared to raw LDPE, indicating that the presence of CS enhances hydration resistance up to a certain extent. This initial increase may be attributed to CS's ability to act as a rigid filler, limiting surface deformation, but as RH increases, hydrated regions begin to form and offset this effect by plasticizing the interface [67].

At 100% RH, however, all LDPE-based composites tend to converge toward similar hardness values, ranging between 47 and 50 units. This indicates that the final plasticizing effect of moisture surpasses composition-related differences, and that under saturation, surface hardness reaches a comparable level across all systems [68].

On the other hand, PS-based composites display globally higher hardness values, ranging from 82 to 85 units, due to the intrinsic stiffness of the amorphous matrix. Although they also exhibit a decrease in hardness with increasing RH—for instance, pure PS drops to around 78 units between 40–80—the reduction is moderate, and a partial recovery is observed around 90% RH, even slightly exceeding the initial value. This 'rebound' behavior could be related to surface reorganization under high moisture, as reported in recent studies on amorphous polymers [69,70].

Additionally, CS-derived PS composites maintain high hardness values even after biopolymer incorporation, and show a less pronounced softening trend. This suggests a favorable interaction between PS and CS that helps preserve mechanical integrity under humid conditions [71,72].

Overall, these results indicate that surface hardness, measured through non-destructive methods, can serve as an indirect indicator of mechanical integrity and moisture behavior. In practical applications, LDPE-CS systems offer less moisture absorption and regulation capacity, but are more prone to surface softening under intermediate RH. In contrast, PS-CS systems remain mechanically more stable, although they exhibit higher moisture absorption.

4. Conclusions

The non-destructive methods applied (XRD, DSC, moisture analysis, and Shore D hardness tests) enabled a comprehensive evaluation of the structural, functional, and mechanical properties of LDPE and PS composites with CS (1 to 5 phr). The incorporation of the biopolymer enhanced the hygroscopic properties in a proportional trend, without causing critical changes in crystallinity, thermal mobility, or surface rigidity. Compared to previous studies, the results obtained are consistent and, in some cases, show advantages by eliminating the need for compatibilizers or destructive testing. The distinct functional profiles observed across the two matrices provide clear guideline for developing active packaging solutions: The 5CSPS formulation is identified as the optimal material for rapid and high-capacity moisture regulation. Due to the amorphous nature of PS, the CS filler creates accessible hydrophilic pathways, resulting in the highest overall water absorption capacity coupled with a high WVTR at saturation. This makes the PS/CS system ideal for applications requiring the material to act as a moisture sink that quickly and efficiently removes excess humidity from the package headspace. The 5CSLDPE formulation offers a distinct advantage for applications requiring enhanced barrier properties with controlled hygroscopicity. Unlike the PS system, LDPE/CS maintained consistently low WVTR values while still showing a four-fold increase in water absorption compared with the pure LDPE. This performance is crucial for packaging that needs to slow down moisture exchange while providing a moderate buffering capacity against humidity fluctuations.

In summary, this research demonstrates that the use of nondestructive techniques enables effective monitoring of the performance of intelligent composite materials, contributing to the development of sustainable and functionally active packaging systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app152111744/s1>, Figure S1: Curves of the LDPE composites; Figure S2. Curves of PS composites; Figure S3. DSC curves of CS: (a) First cycle; and (b) Second cycle; Figure S4. DSC first cycle curves of: (a) LDPE; (b) 1CSLDPE; (c) 3CSLDPE; and (d) 5CSLDPE; Figure S5. DSC first cycle curves of PS composites.

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Abbreviations

The following abbreviations are used in this manuscript:

RH	Relative Humidity
CS	Chitosan
PLA	Polylactic Acid
PCL	Polycaprolactone
LDPE	Low Density Polyethylene
PS	Polystyrene
PVA	Poly (Vinyl Alcohol)
XRD	X-ray Diffraction
DSC	Differential Scanning Calorimetry
WVT	Water Vapor Transmission
MFI	Melt Flow Index
RPM	Revolutions Per Minutes
PHR	Per Hundred Resins
TGA	Thermogravimetry
kV	Kilovolts
mA	Milliamperes
ICDD	International Centre for Diffraction Data
T _g	Glass Transition Temperature
T _m	Melting Temperature
T _c	Crystallization Temperature
ΔH _m	Melting enthalpy
ΔH _c	Crystallization enthalpy
χ _c	Percentage of crystallinity
ΔH ₁₀₀	100% crystalline polyethylene enthalpy
%Abs	Percentage of absorption
D	Water Diffusion Coefficient
%SML	Percentage of Soluble Materia Loss
ASTM	American Standard for Testing and Materials
WW	Wet Weight
DW	Dry Weight
IW	Initial Weight
D ₀	Uncorrected water diffusion coefficient
H	Height
%M	Percentage of Moisture
T	Time
L	Length
W	Wide
WG	Weight Gained
A	Area
HD	Hardness
T _{onset}	Initial Degradation Temperature
T _{max}	Maximum Degradation Temperature
T _p	Processing Temperature

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