

Article

Data-Assisted Mechanical Balance Screening of and Candidate Window Identification for Starch/Halloysite Nanotube-Modified Cow Dung-Based Biodegradable Films

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Featured Application

This study provides a screening-stage, data-assisted strategy for identifying mechanically balanced candidate formulations of cow dung-based biodegradable covering films. The workflow combines experimental screening, SEM-supported surface morphology verification, local trend mapping, and independent validation of previously untested candidate compositions, thereby supporting the prioritization and refinement of starch/HNT formulation regions for agricultural covering materials.

Abstract

Agricultural waste-based biodegradable films are promising alternatives to polyethylene mulch films, but their use is limited by insufficient mechanical stability and the difficulty of balancing strength, ductility, and stiffness. In this study, cow dung-based biodegradable films were modified with cationic starch and halloysite nanotubes (HNTs) through a brush-coating process. SEM observations of pristine HNTs, the uncoated substrate, the starch-coated control, and the representative starch/HNT composite film provided morphological evidence for starch coating formation and HNT incorporation into the surface layer. Fifteen initial formulations were evaluated using tensile strength, elongation at break, apparent tensile modulus, a normalized mechanical balance score, and weighting sensitivity analysis. The highest values of the three mechanical indicators occurred at different formulations, indicating that formulation selection should be treated as a mechanical balance problem rather than a single-property maximization task. F14 showed the most stable overall mechanical balance among the tested formulations. SVR and GBR models were then used as bounded auxiliary tools for local trend mapping, with LOOCV R^2 values of 0.679, 0.855, and 0.856 for tensile strength, elongation at break, and apparent tensile modulus, respectively. A desirability-based consensus analysis identified a high-potential window at approximately 2.30–2.50 wt% starch and 1.25–1.75 wt% HNT. Four previously untested formulations selected from this frozen model-defined region were independently prepared and experimentally validated, showing good prediction–experiment consistency within the candidate window. Preliminary soil burial observation further indicated progressive macroscopic structural deterioration of F14 during prolonged soil exposure, although this result was interpreted only as qualitative appearance evidence. Overall, the proposed workflow provides an experimentally bounded decision-support strategy for prioritizing mechanically balanced starch/HNT-modified cow dung-based biodegradable film formulations.

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Keywords: cow dung-based biodegradable film; cationic starch; halloysite nanotubes; mechanical balance screening; data-assisted trend mapping; desirability; consensus high-potential window; candidate window identification

1. Introduction

Conventional polyethylene (PE) mulching can provide important agronomic benefits, but its persistence and end-of-life residues have raised concerns regarding soil quality and ecosystem effects [1–7]. Biodegradable polymer films such as PLA-, PBAT-, starch-, and cellulose-based materials have been investigated as alternatives to PE mulch films [8–15]. These materials show improved environmental compatibility, but their large-scale agricultural application may still be limited by cost, feedstock dependence, water sensitivity, or insufficient mechanical durability. In contrast, agricultural waste-based biodegradable films can reduce raw material costs while promoting biomass waste utilization [16–20]. Cow dung is a large-volume livestock waste containing cellulose, hemicellulose, and lignin. Beyond its traditional use as fertilizer or soil amendment, cow dung has also been explored as a biomass resource for cow dung-derived cellulose fibers, paper-like substrates, and agricultural covering materials, indicating its potential for higher-value utilization [21–24]. Nevertheless, cow dung-based films still require further improvement in mechanical performance and formulation stability before practical use.

Cationic starch and halloysite nanotubes (HNTs) are promising modifiers for biomass-based film systems. Cationic starch is renewable, biodegradable, and film-forming and can act as a surface-sizing or interfacial integration component in cellulose-rich materials [8,24]. HNTs are naturally occurring tubular aluminosilicate nanoclays with a hollow lumen and chemically differentiated external siloxane-rich and internal aluminol-rich surfaces. Their tubular morphology, aspect ratio, surface reactivity, and capacity to host or support functional species make them useful as reinforcing fillers, adsorption media, carrier materials, and supports for functional components in polymer and bio-based composites [25,26]. In film systems, however, the effect of HNTs depends strongly on their loading level, dispersion state, and interaction with the surrounding matrix. Excessive HNT addition may lead to local agglomeration or stress concentration rather than further property improvement.

From a green materials and circular economy perspective, combining naturally occurring clay nanotubes with biomass-derived polysaccharides or cellulose fibers provides a route for integrating mineral resources with renewable or waste-derived feedstocks. HNT–biomass composites have therefore been explored for sustainable films, packaging materials, adsorption and remediation systems, and other functional materials [25,27]. Beyond materials applications, the hollow structure and tunable surface chemistry of HNTs have also motivated research in catalytic supports, controlled-release systems, and biomedical applications [26,28,29]. Since the present study does not evaluate HNT release, exposure, migration, or toxicological effects, no health safety claim is made. Here, HNTs are considered mineral nanofillers incorporated into a water-based starch coating for agricultural waste-based film modification.

Beyond starch-based matrices, HNTs have also been incorporated into PLA films to modify the mechanical, thermal, and barrier-related properties of biodegradable polymer films [30–32]. Representative starch/HNT-based biodegradable films have mainly been developed as relatively homogeneous starch, thermoplastic starch, or starch blend matrices. HNTs have been incorporated into thermoplastic starch films, PVA/starch-based packaging films, and potato starch composite films to improve mechanical, water resistance, barrier, or flame-retardant performance [33–35]. In addition, recent work has

combined artificial neural networks, multi-objective genetic algorithms, and TOPSIS to optimize mechanical, barrier, and optical properties in PLA/PBAT nanoclay packaging films containing HNTs and other clays [36]. These studies demonstrate the value of HNTs as naturally occurring mineral nanofillers, but their material configurations, application scenarios, and formulation design objectives differ from those of the present study.

The present system is not a homogeneous starch-based or thermoplastic starch matrix. Instead, it consists of a cow dung pulp-containing cellulose substrate modified by a starch/HNT surface-coating process. In such a fiber-network-based substrate, the coating layer and the underlying cellulose network may jointly influence tensile behavior. More importantly, the central question of this study is not whether a single starch/HNT formulation can maximize one individual property. The measured tensile strength, elongation at break, and apparent tensile modulus showed favorable values at different starch/HNT compositions. Therefore, direct comparison of discrete experimental formulations can identify single-property maxima, but cannot by itself prioritize nearby untested compositions with a more balanced mechanical profile. This creates a bounded formulation selection problem rather than a simple single-factor reinforcement problem.

Accordingly, the original fifteen screening formulations were first evaluated using a normalized mechanical balance score and weighting sensitivity analysis to distinguish mechanically balanced formulations from single-property optima. SEM characterization was introduced to provide surface morphological evidence for starch coating formation and HNT incorporation into the representative composite film. Data-assisted modeling methods have been increasingly used to analyze composition–property relationships and visualize local response trends in materials research [37,38]. However, under small-sample or sparse-data conditions, such models should be used cautiously as auxiliary tools for organizing measured results, visualizing local trends, and identifying candidate regions, rather than as independent optimization methods replacing experimental validation [39,40]. SVR and GBR models were therefore used only for local trend mapping within the experimentally investigated composition range. A desirability-based consensus analysis converted the separate mechanical response maps into a candidate window for formulation prioritization. Importantly, four previously untested formulations selected from the frozen model-defined candidate region were subsequently prepared and independently tested; these validation formulations were not included in model fitting, LOOCV evaluation, model selection, or candidate window construction. Therefore, the contribution of this study is threefold: (i) evaluation and morphological verification of starch/HNT surface modification for a cow dung pulp-containing cellulose substrate intended for biodegradable agricultural covering materials; (ii) distinction between single-property optima and mechanically balanced formulations; and (iii) development and independent experimental assessment of a data-assisted but experimentally bounded candidate window workflow for prioritizing subsequent formulation refinement.

2. Materials and Methods

2.1. Materials and Equipment

2.1.1. Raw Materials and Reagents

The raw materials used in this study included cow dung pulp board, paper pulp board, cationic starch, halloysite nanotubes (HNTs), and deionized water. Their suppliers, available specification information, functions in this study, and notes are summarized in Table 1. The cow dung pulp board was used as the main biomass fiber component for constructing the biodegradable substrate, while paper pulp board was used as an auxiliary cellulose source to improve sheet formation and structural continuity. Cationic starch was used as a biodegradable film-forming and surface-sizing component, and HNTs were

used as inorganic nanotubular fillers to regulate the mechanical response within the starch/HNT formulation window.

Only supplier-provided or literature-supported material information was used in this study, and parameters not available for the present material batches were not used as formulation variables. All materials were used as received unless otherwise stated.

In this study, “cow dung-based” refers to a cow dung pulp-containing cellulose substrate prepared with auxiliary paper pulp to improve sheet formation and structural continuity. The auxiliary paper pulp was used to reduce substrate heterogeneity during film preparation.

Table 1. Raw materials used in this study and available material information.

Material	Supplier/Source	Available Information	Function in This Study	Notes
Paper pulp board	Changsha Furong District Subei Trading Company, Changsha, China	Commercial cellulose pulp board. Detailed fiber length, pulping degree, and lignin content were not provided by the supplier.	Auxiliary cellulose source for improving sheet formation and reducing substrate heterogeneity.	Used as received.
	Dongguan Dongmei Food Co., Ltd., Dongguan, China	Commercial cationic starch, model DM-933; supplied as white powder.	Film-forming and surface-sizing component for forming the coating layer and improving substrate integration.	
Halloysite nanotubes (HNTs)	Hunan Guzhang County Linshiyu Mineral Products Co., Ltd., Guzhang, China	Halloysite powder; purity 99.5%; CAS No. 1332-58-7.	Inorganic nanotubular filler for regulating mechanical response within the starch/HNT formulation window.	Tube length, outer diameter, and specific surface area were not available; magnetic stirring was used for dispersion.
Cow dung pulp board	Zhangye Huarui Agricultural Co., Ltd., Zhangye, China	Cow dung-derived lignocellulosic pulp board. Previous studies using the same research route reported cellulose, hemicellulose, and lignin components in cow dung fibers [21,22].	Main biomass fiber component for preparing the biodegradable substrate.	Batch-specific fiber morphology and composition were not re-measured in this study.

Table note: Only supplier-provided or literature-based material information is listed. Parameters not independently measured in this study were not used as formulation variables.

2.1.2. Main Equipment

Table 2 lists the main equipment used for suspension preparation, drying, conditioning, weighing, and tensile testing. This information is provided to improve the reproducibility of the experimental procedure.

Table 2. Main equipment used in this study.

Equipment	Model/Description	Manufacturer	Application in This Study
Sheet former	TD10-200	Xianyang Tongda Light Industry Equipment Co., Ltd., Xianyang, China	Preparation of cow dung-based substrate sheets
Analytical balance	FA1004N	Changzhou Xingyun Electronic Equipment Co., Ltd., Changzhou, China	Weighing of raw materials and coating components
Constant-temperature magnetic stirrer	MS-H280-Pro	DLAB Scientific Co., Ltd., Beijing, China	Preparation of cationic starch solution and starch/HNT coating suspension
Drying oven	DHG-09030A	Shanghai Hongdu Electronic Technology Co., Ltd., Shanghai, China	Drying of coated films
Universal tensile testing machine	YH-L-200A	Dongguan Huitai Instrument Machinery Co., Ltd., Dongguan, China	Measurement of tensile strength, elongation at break, and apparent tensile modulus
Constant temperature and humidity chamber	LHS-250HC-II	Shanghai Yiheng Scientific Instrument Co., Ltd., Shanghai, China	Conditioning of film samples before mechanical testing

2.2. Formulation Design and Sample Coding

Fifteen initial formulations were designed to establish the original mechanical screening dataset for mechanical balance analysis and data-assisted trend mapping. The sample set included one blank control, two single-component controls, and twelve starch/HNT composite formulations. The detailed formulation design is shown in Table 3.

F01 was the unmodified cow dung-based substrate. F02 was the starch-only coated control with 2.0 wt% cationic starch, and F03 was the HNT-only coated control with 1.0 wt% HNT. The composite formulations F04–F15 were arranged within a two-factor formulation window, including three starch levels (1.5, 2.0, and 2.5 wt%) and four HNT levels (0.5, 1.0, 1.5, and 2.0 wt%). For the starch/HNT composite formulations, the HNT level was defined relative to the starch solid content. This design enabled comparison of the effects of starch-only treatment, HNT-only treatment, and starch/HNT composite modification under a unified coating process.

For F04–F15, the HNT level was calculated relative to the dry mass of cationic starch, while F03 was used as a nominal HNT-only control for comparison.

Table 3. Formulation design and sample coding.

Formulation Code	Sample Type	Treatment Method	Starch Content (wt%)	HNT Level (wt%)
F01	Blank control	None	0.0	0.0
F02	Starch-only modified control	Brush coating	2.0	0.0
F03	HNT-only control	Brush coating	0.0	1.0
F04	Composite screening group	Brush coating	1.5	0.5
F05	Composite screening group	Brush coating	1.5	1.0
F06	Composite screening group	Brush coating	1.5	1.5
F07	Composite screening group	Brush coating	1.5	2.0
F08	Composite screening group	Brush coating	2.0	0.5
F09	Composite screening group	Brush coating	2.0	1.0
F10	Composite screening group	Brush coating	2.0	1.5
F11	Composite screening group	Brush coating	2.0	2.0
F12	Composite screening group	Brush coating	2.5	0.5
F13	Composite screening group	Brush coating	2.5	1.0
F14	Composite screening group	Brush coating	2.5	1.5
F15	Composite screening group	Brush coating	2.5	2.0

V1	Independent validation formulation	Brush coating	2.5	1.6
V2	Independent validation formulation	Brush coating	2.5	1.3
V3	Independent validation formulation	Brush coating	2.4	1.5
V4	Independent validation formulation	Brush coating	2.4	1.7

Table note: F01–F15 constituted the original screening dataset used for mechanical balance analysis and model development. V1–V4 were independently prepared after candidate window identification and were not included in model fitting, LOOCV, model selection, or desirability window construction. For all starch/HNT composite and validation formulations, HNT level was defined relative to the dry mass of cationic starch.

After the consensus candidate window had been identified from the original screening dataset, four additional starch/HNT formulations were prepared for independent experimental validation. These formulations were denoted as V1–V4 and were not included in model development, hyperparameter selection, LOOCV evaluation, or desirability-based window construction. Their compositions are also listed in Table 3.

2.3. Preparation of Cow Dung-Based Films and Surface Modification

2.3.1. Preparation of the Base Film

Cow dung-based substrate films were prepared using a paper sheet-forming process. Cow dung pulp board and paper pulp board were separately dispersed in deionized water to obtain uniform fiber slurries. The two slurries were then mixed at a mass ratio of 4:6 (cow dung pulp:paper pulp). The mixed slurry was formed into sheets using a TD10-200 sheet former (Xianyang Tongda Light Industry Equipment Co., Ltd., Xianyang, China). To meet the requirements of surface modification and mechanical screening, the basis weight of the substrate film was controlled at approximately 80 g m⁻². After sheet formation, the substrate films were conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for at least 24 h before surface treatment.

2.3.2. Preparation of the Cationic Starch/HNT Composite Modification Solution

Cationic starch/HNT coating suspensions were prepared according to the formulation design listed in Table 3. In this study, 100 g of working coating suspension was prepared for each formulation. The HNT level in the composite samples was defined as the mass fraction of HNT relative to the dry mass of cationic starch solids:

$$H = \frac{m_{\text{HNT}}}{m_{\text{starch}}} \times 100\% \quad (1)$$

where H is the HNT level (wt%), m_{HNT} is the mass of added HNT, and m_{starch} is the dry mass of cationic starch solids. For the HNT-only control F03, no cationic starch was added; therefore, the listed HNT level was used only as a nominal treatment level for comparison with the composite formulations.

The detailed weighing amounts for 100 g of coating suspension are listed in Table 4. For starch-containing formulations, the required amount of cationic starch was first added to deionized water and heated to 85–90 °C with magnetic stirring for approximately 30 min until a uniform starch solution without visible particles was obtained. The starch solution was then cooled to approximately 50–60 °C before HNT addition. For starch/HNT composite and validation formulations, the designed amount of HNT powder was gradually added to the starch solution with continuous magnetic stirring, and the mixture was further stirred for 15–20 min to obtain a uniform coating suspension. In this study, HNT

dispersion was performed by magnetic stirring rather than ultrasonication. For the HNT-only control F03, HNT powder was directly dispersed in deionized water under the same magnetic stirring conditions.

Table 4. Weighing amounts for preparing 100 g of coating suspension.

Sample Code	Cationic Starch (g)	HNT (g)	Deionized Water (g)	Coating Suspension Type
F01	-	-	-	No coating suspension
F02	2.0000	0	98.0000	Starch solution
F03	0	0.0200	99.9800	HNT aqueous dispersion
F04	1.5000	0.0075	98.4925	Starch/HNT suspension
F05	1.5000	0.0150	98.4850	Starch/HNT suspension
F06	1.5000	0.0225	98.4775	Starch/HNT suspension
F07	1.5000	0.0300	98.4700	Starch/HNT suspension
F08	2.0000	0.0100	97.9900	Starch/HNT suspension
F09	2.0000	0.0200	97.9800	Starch/HNT suspension
F10	2.0000	0.0300	97.9700	Starch/HNT suspension
F11	2.0000	0.0400	97.9600	Starch/HNT suspension
F12	2.5000	0.0125	97.4875	Starch/HNT suspension
F13	2.5000	0.0250	97.4750	Starch/HNT suspension
F14	2.5000	0.0375	97.4625	Starch/HNT suspension
F15	2.5000	0.0500	97.4500	Starch/HNT suspension
V1	2.5000	0.0400	97.4600	Starch/HNT suspension
V2	2.5000	0.0325	97.4675	Starch/HNT suspension
V3	2.4000	0.0360	97.5640	Starch/HNT suspension
V4	2.4000	0.0408	97.5592	Starch/HNT suspension

Table note: For F04–F15 and V1–V4, HNT was calculated relative to the dry mass of cationic starch. For F03, the HNT amount was set as a nominal HNT-only treatment level equivalent to 1.0 wt% of the starch solid mass used in the 2.0 wt% starch formulation.

2.3.3. Brush Coating, Drying, and Conditioning

Except for the blank control F01, all surface-modified samples were treated using the brush-coating method. F02 was coated with the cationic starch solution, F03 was coated with the HNT aqueous dispersion, and F04–F15 and V1–V4 were coated with the starch/HNT composite suspensions. The coating suspension was uniformly applied to both sides of the cow dung-based substrate film. The target wet coating add-on was controlled at 95 g m⁻² and was calculated as

$$W_{\text{add-on}} = \frac{m_1 - m_0}{A} \quad (2)$$

where $W_{\text{add-on}}$ is the wet coating add-on per unit area (g m⁻²), m_0 is the mass of the substrate before coating, m_1 is the mass of the sample immediately after wet coating, and A is the total coated area of both film surfaces.

After coating, all surface-treated samples were dried in a drying oven at 75 °C for 70 min. The dried films were then conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for 24 h before mechanical testing and data acquisition. The same coating, drying, and conditioning procedure was applied to all modified samples to reduce process-induced differences among formulation groups. The overall preparation process is illustrated in Figure 1.

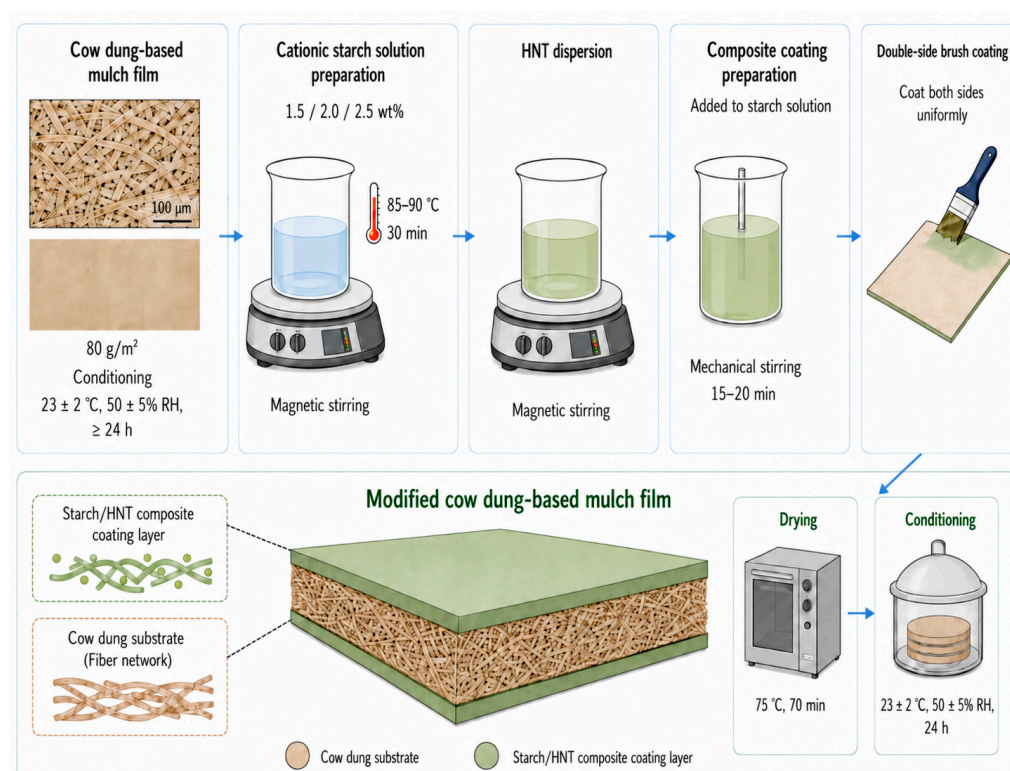


Figure 1. Preparation process of starch/HNT-modified cow dung-based biodegradable films.

2.4. Scanning Electron Microscopy (SEM)

The surface morphologies of pristine halloysite nanotubes (HNTs), the uncoated cow dung-based substrate (F01), the starch-coated control film (F02), and the representative starch/HNT-coated film (F14) were examined using a scanning electron microscope (ZEISS Gemini SEM 300, Carl Zeiss Microscopy GmbH, Jena, Germany). Before observation, all specimens were subjected to gold sputtering treatment to improve surface conductivity.

Pristine HNT powder was observed at magnifications of 10,000× and 20,000× to identify its characteristic particle morphology. The surfaces of F01, F02, and F14 were examined at appropriate magnifications for comparison of the substrate, starch-coated surface, and starch/HNT-coated surface. The accelerating voltage and corresponding scale bars are indicated in the SEM micrographs. F14 was selected as the representative starch/HNT-coated formulation because it exhibited a balanced mechanical performance among the experimentally tested formulations.

2.5. Mechanical Testing and Statistical Analysis

The mechanical properties of all film samples were evaluated by uniaxial tensile testing. Before testing, all samples were conditioned at 23 ± 2 °C and $50 \pm 5\%$ relative humidity for 24 h. Rectangular specimens with dimensions of 2 cm × 10 cm were cut from the uniform central region of each film, while edge regions with possible fiber distribution heterogeneity were avoided. For each formulation, three parallel specimens were tested. Tensile testing was performed using a YH-L-200A universal tensile testing machine (Dongguan Huitai Instrument Machinery Co., Ltd., Dongguan, China). The gauge length was set to 50 mm, and the crosshead speed was 5 mm min^{−1}. The tensile force and displacement were recorded during testing. Tensile strength, elongation at break, and apparent tensile modulus were used as the main mechanical indicators in this study. Tensile strength was calculated as

$$\sigma = \frac{F_{\max}}{A_0} \quad (3)$$

where σ is the tensile strength (MPa), $F_{\max}$ is the maximum tensile force before fracture (N), and A_0 is the initial cross-sectional area of the specimen (mm²). The initial cross-sectional area was calculated from the specimen width and the average pre-test film thickness. The thickness of each specimen was measured at several positions along the strip, and the average value was used for cross-sectional area calculation.

Elongation at break was calculated as

$$\varepsilon_b = \frac{L_b - L_0}{L_0} \times 100\% \quad (4)$$

where ε_b is the elongation at break (%), L_0 is the initial gauge length (mm), and L_b is the gauge length at fracture (mm).

The apparent tensile modulus was obtained from the initial linear region of the stress-strain curve:

$$E_{\text{app}} = \frac{\Delta\sigma}{\Delta\varepsilon} \quad (5)$$

where E_{app} is the apparent tensile modulus (MPa), and $\Delta\sigma/\Delta\varepsilon$ is the slope of the selected initial linear elastic region of the stress-strain curve.

All mechanical results were expressed as mean $\pm$ standard deviation. Error bars in the figures represent standard deviations of parallel specimens. The standard deviation was calculated as

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (6)$$

where s is the standard deviation, x_i is each individual measurement, $\bar{x}$ is the mean value, and n is the number of parallel specimens. The same preparation, conditioning, tensile-testing, and data-processing procedures were applied to V1–V4 to ensure comparability with the original screening formulations.

For data-assisted trend mapping and mechanical balance scoring, only the mean mechanical properties of the original fifteen screening formulations were used as formulation-level input data. The validation results of V1–V4 were retained as an independent test set until prediction–experiment comparison was completed.

2.6. Mechanical Balance Score and Weighting Sensitivity

To compare the overall mechanical performance of different formulations, tensile strength, elongation at break, and apparent tensile modulus were integrated using a normalized mechanical balance score. Because the three mechanical indicators have different units and numerical ranges, each indicator was first normalized using min-max normalization:

$$X_{ij}^* = \frac{X_{ij} - X_{j,\min}}{X_{j,\max} - X_{j,\min}} \quad (7)$$

where X_{ij}^* is the normalized value of the j -th mechanical indicator for the i -th sample, X_{ij} is the measured value, and $X_{j,\min}$ and $X_{j,\max}$ are the minimum and maximum measured values of the j -th indicator among the original fifteen screening formulations, respectively. In this screening-stage study, tensile strength, elongation at break, and apparent tensile modulus were all treated as positive mechanical response indicators within the tested formulation window.

The mechanical balance score was calculated as

$$S_i = w_1 X_{i,\text{TS}}^* + w_2 X_{i,\text{EB}}^* + w_3 X_{i,\text{M}}^* \quad (8)$$

where S_i is the mechanical balance score of the i -th sample, $X_{i,TS}^*$, $X_{i,EB}^*$, and $X_{i,M}^*$ are the normalized tensile strength, elongation at break, and apparent tensile modulus, respectively, and w_1 , w_2 , and w_3 are the corresponding weights.

In the main analysis, equal weights were used as a neutral baseline. This equal-weight score was not intended to represent a universal engineering optimum for all agricultural service conditions. Instead, it was used to provide a simple and transparent comparison of the tested samples when no specific mechanical property was assigned priority. In this study, $w_1 = w_2 = w_3 = 1/3$.

To reduce the arbitrariness of weight selection, a weighting sensitivity analysis was also conducted using three alternative schemes. The strength-priority scheme emphasized tensile resistance, the ductility-priority scheme emphasized deformation tolerance, and the stiffness-priority scheme emphasized modulus-related dimensional stability. The weight settings are listed in Table 5.

Table 5. Weighting schemes used for mechanical balance evaluation.

Weighting Scheme	Tensile Strength	Elongation at Break	Apparent Tensile Modulus
Equal-weight baseline	1/3	1/3	1/3
Strength-priority scheme	0.50	0.25	0.25
Ductility-priority scheme	0.25	0.50	0.25
Stiffness-priority scheme	0.25	0.25	0.50

The ranking obtained from the equal-weight score was used as the primary mechanical balance result, while the alternative weighting schemes were used only to assess whether the identified favorable formulation remained competitive with different mechanical priorities. Therefore, the mechanical balance score should be interpreted as a relative screening index within the present sample set, rather than an absolute performance criterion for all field applications.

2.7. Data-Assisted Trend Mapping

Data-assisted trend mapping was used as an auxiliary method to organize the measured mechanical data, visualize local formulation-dependent responses, and support formulation region prioritization within the tested composition space. It was not intended to replace experimental validation, extrapolate beyond the tested composition range, or determine a universal optimum formulation. This treatment follows the small-data nature of experimental materials studies, in which model outputs should be interpreted together with measured data and used primarily for local trend interpretation rather than for standalone predictive optimization [39–41]. The overall workflow is shown in Figure 2, including dataset construction, model training, LOOCV evaluation, response-map generation, variable-contribution analysis, and candidate-region interpretation.

The input variables were cationic starch content and HNT level, and the output variables were tensile strength, elongation at break, and apparent tensile modulus. Each mechanical property was modeled separately using the original fifteen screening formulations (F01–F15) listed in Table 3. The input vector of the i -th sample was defined as

$$x_i = [C_i, H_i] \quad (9)$$

where x_i is the input vector of the i -th sample, C_i is the cationic starch content, and H_i is the HNT level. For the blank and single-component control samples, the corresponding missing component was coded as zero according to the formulation design.

Because support vector regression is sensitive to the scale of input variables, z-score standardization was applied to the input variables before model training. To keep the input format consistent across models, the same standardized inputs were also used for gradient boosting regression. The standardized value was calculated as

$$z_i = \frac{x_i - \mu}{s} \quad (10)$$

where x_i is the original value of the input variable, μ is the mean value of that variable in the training set, s is the corresponding standard deviation, and z_i is the standardized value. During LOOCV, μ and s were calculated from the training samples in each fold and then applied to the left-out validation sample.

Support vector regression (SVR) and gradient boosting regression (GBR) were used to construct the auxiliary mapping models. These two models were selected because they can capture nonlinear composition–property relationships without requiring a fixed linear response assumption. In this study, tensile strength was modeled using SVR with a radial basis function (RBF) kernel, while elongation at break and apparent tensile modulus were modeled using GBR.

The general prediction form of SVR can be expressed as

$$\hat{y} = \sum_{i=1}^n (\alpha_i - \alpha_i^*) K(x_i, x) + b \quad (11)$$

where $\hat{y}$ is the predicted value, $K(x_i, x)$ is the kernel function, α_i and α_i^* are Lagrange multipliers, b is the bias term, and n is the number of training samples. In this study, the RBF kernel was used to describe local nonlinear trends in the formulation–property relationship.

The prediction form of GBR can be expressed as

$$\hat{y} = F_0(x) + \sum_{m=1}^M \eta h_m(x) \quad (12)$$

where $\hat{y}$ is the predicted value, $F_0(x)$ is the initial model, M is the number of weak learners, η is the learning rate, and $h_m(x)$ is the m -th regression tree learner. By sequentially fitting residual errors, GBR can describe nonlinear response patterns within the tested formulation range.

Considering the limited sample size, the models were used only for local trend visualization and relative response comparison. No extrapolative prediction outside the investigated starch/HNT formulation window was performed, because model interpretation should be restricted to the applicable composition domain under small-data conditions [39,41]. Leave-one-out cross-validation (LOOCV) was used to evaluate the stability of the trend-mapping models under small-sample conditions. In each LOOCV cycle, one sample was left out as the validation sample, while the remaining samples were used for model fitting. This process was repeated until each sample had been used once as the validation sample.

Model performance was evaluated using the coefficient of determination (R^2) and root mean square error (RMSE):

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (13)$$

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (14)$$

where y_i is the measured value, $\hat{y}_i$ is the LOOCV-predicted value, $\bar{y}$ is the mean measured value, and n is the number of samples. The model with more stable LOOCV performance was used to generate response maps for the corresponding mechanical property.

For response map visualization, the starch/HNT formulation space was divided into a dense grid within the tested composition range. The trained models then estimated the relative response distribution across this local grid. The resulting maps were interpreted together with the measured data rather than as independent evidence of optimality.

Permutation importance was used to describe the relative sensitivity of each mechanical property model to starch content and HNT level. For each input variable, its values were randomly shuffled, and the resulting decrease in model performance was used to estimate its relative contribution. The contribution values of starch content and HNT level were normalized to 100% for each target property. This analysis was used only to describe model sensitivity and should not be interpreted as direct causal or mechanistic evidence.

In addition to generating single-property response maps, the model-predicted mechanical responses served as inputs for desirability-based candidate window identification. This additional step translated separate response maps into a multi-objective screening region under different mechanical priorities. The detailed desirability-based consensus procedure is described in Section 2.8.

All data-assisted analyses were performed using Python 3.13.9 with scikit-learn 1.7.2, NumPy 2.3.5, pandas 2.3.3, and Matplotlib 3.10.6. The final model settings are summarized in Table 6, and the corresponding LOOCV performance values are presented in Section 3.

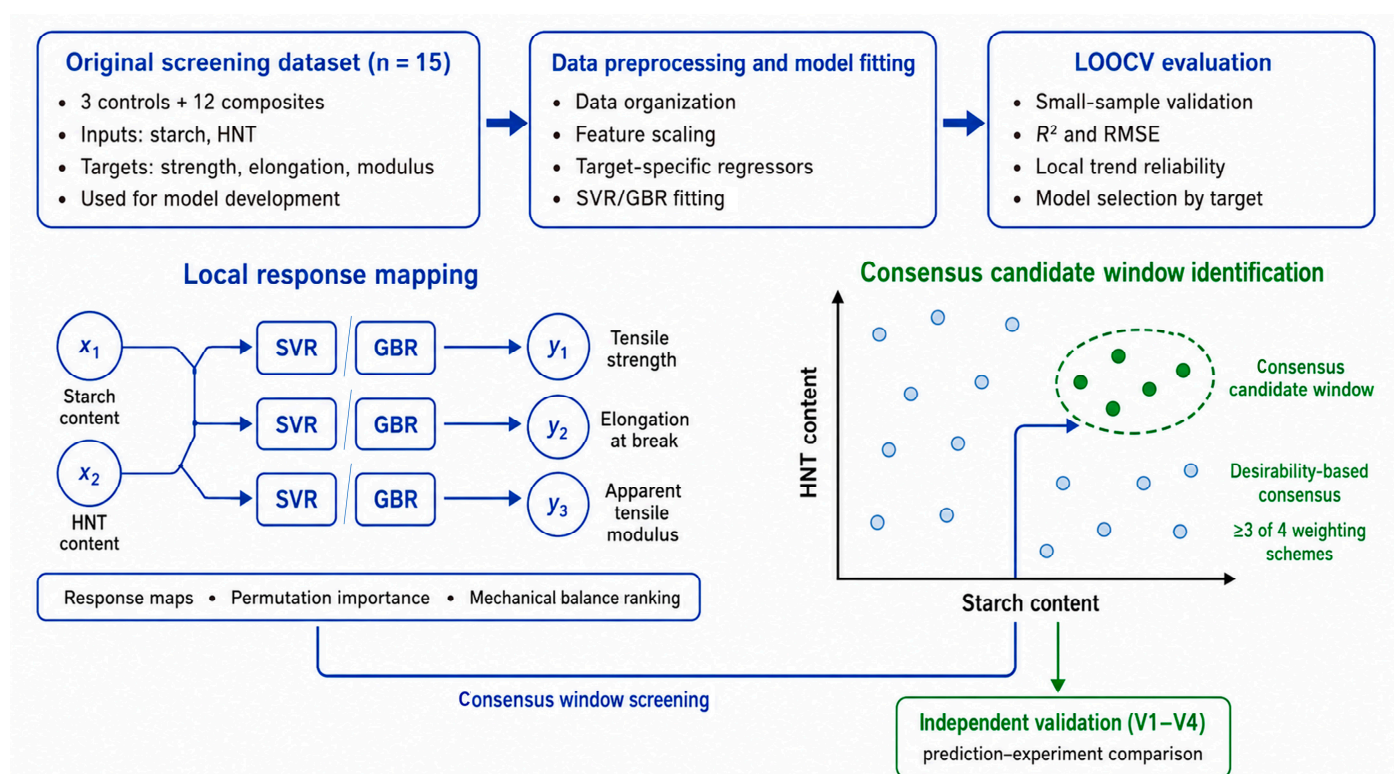


Figure 2. Workflow of data-assisted trend mapping and formulation screening. Arrows indicate the direction of the data-processing and screening workflow. Blue open circles represent other grid points in the screened formulation space, whereas green filled circles represent consensus high-potential grid points supported by at least three of the four weighting schemes; the dashed green ellipse indicates the Consensus candidate window.

Table 6. Model settings used for data-assisted trend mapping.

Mechanical Property	Selected Model	Main Parameter Settings	Validation Method	Evaluation Metrics
Tensile strength	SVR with RBF kernel	C = 100; gamma = scale; epsilon = 0.0005; n_estimators = 50;	LOOCV	R ² , RMSE
Elongation at break	Gradient boosting regression	max_depth = 2; learning_rate = 0.15; min_samples_leaf = 1; n_estimators = 200;	LOOCV	R ² , RMSE
Apparent tensile modulus	Gradient boosting regression	max_depth = 2; learning_rate = 0.15; min_samples_leaf = 3	LOOCV	R ² , RMSE

2.8. Desirability-Based Consensus Window Identification

To further translate the model-predicted mechanical response maps into actionable guidance for formulation screening, a desirability-based consensus analysis was conducted within the tested starch/HNT composite formulation window. The desirability approach has been widely used for integrating multiple response variables by converting individual responses into comparable desirability values and combining them into an overall desirability score [42]. In the present study, this analysis was used only for candidate window prioritization and should not be interpreted as the direct determination of an absolute optimum formulation.

For each grid point in the predicted formulation space, tensile strength, elongation at break, and apparent tensile modulus were first converted into individual desirability values. Because all three mechanical indicators were treated as positive response variables in the present screening-stage study, a larger-the-better desirability function was used:

$$d_j(y) = \begin{cases} 0, & y \leq L_j \\ \left(\frac{y - L_j}{U_j - L_j}\right)^{s_j}, & L_j < y < U_j \\ 1, & y \geq U_j \end{cases} \quad (15)$$

where $d_j(y)$ is the desirability value of the j -th mechanical indicator, y is the predicted value at a given grid point, L_j and U_j are the lower and upper reference limits, respectively, and s_j is the shape parameter. In this study, s_j was set to 1.0 for all three indicators. To reduce the influence of extreme measured values, L_j and U_j were defined using the 10th and 90th percentiles of the measured values of each mechanical indicator among the original fifteen screening formulations, respectively.

The overall desirability score under a given weighting scheme was calculated using a weighted geometric mean:

$$D_k = (d_{TS}^{w_{TS,k}} \cdot d_{EB}^{w_{EB,k}} \cdot d_M^{w_{M,k}})^{1/(w_{TS,k} + w_{EB,k} + w_{M,k})} \quad (16)$$

where D_k is the overall desirability score under the k -th weighting scheme, and d_{TS} , d_{EB} , and d_M are the individual desirability values of tensile strength, elongation at break, and apparent tensile modulus, respectively. The parameters $w_{TS,k}$, $w_{EB,k}$, and $w_{M,k}$ represent the corresponding weights assigned to tensile strength, elongation at break, and apparent tensile modulus, respectively, under the k -th weighting scheme. The same four weighting schemes used in the measured mechanical balance analysis were adopted, including the equal-weight, strength-priority, ductility-priority, and stiffness-priority schemes.

For each weighting scheme, the maximum desirability score $D_{k,max}$ was identified, and grid points satisfying $D_k \geq 0.85 D_{k,max}$ were regarded as high-potential points under

that scheme. A grid point was further defined as belonging to the consensus high-potential window only when it was supported by at least three of the four weighting schemes. The $0.85 D_{k,max}$ threshold and the three-of-four weighting consensus rule were used as conservative screening criteria to identify formulation regions that remained favorable under different mechanical priorities, rather than regions favored by a single weighting assumption. These criteria were not intended to define a mathematically unique optimum formulation. The resulting consensus window was used as a model-assisted priority region for subsequent experimental validation.

2.9. Independent Experimental Validation Design

To assess the practical consistency of the model-guided candidate region, four previously untested formulations were selected after the original model development and consensus window construction had been completed. The models, desirability reference bounds, weighting schemes, and consensus thresholds were fixed before fabrication of the validation samples. V1 (2.5 wt% starch, 1.6 wt% HNT), V2 (2.5 wt% starch, 1.3 wt% HNT), V3 (2.4 wt% starch, 1.5 wt% HNT), and V4 (2.4 wt% starch, 1.7 wt% HNT) were selected from the largest consensus high-potential region. These formulations were not included in model training, LOOCV evaluation, parameter selection, or desirability window construction. The films were prepared and tested using the same procedures described above, with three parallel specimens tested for each formulation.

2.10. Preliminary Indoor Soil Burial Observation and Endpoint Macroscopic Recording

A preliminary indoor soil burial observation was conducted to examine the macroscopic structural changes of the representative mechanically favorable formulation under soil contact conditions. This test was designed as an application-oriented appearance observation rather than a complete quantitative biodegradation or mineralization assay. Therefore, the results were used to evaluate visible changes in film integrity and covering continuity.

Film specimens used for different tests were prepared with test-specific dimensions. For the preliminary indoor soil burial observation, F14 specimens were separately prepared using the same film preparation procedure but with a larger circular geometry. Specifically, circular F14 specimens with a diameter of approximately 15 cm were used to fit the soil container and to facilitate macroscopic observation of film-covering integrity during burial. Loose farmland soil was sieved to remove stones, plant residues, and coarse impurities. The specimens were placed in moist soil under indoor conditions, and soil moisture was adjusted periodically to prevent complete drying. The burial observation was conducted at room temperature.

The macroscopic appearance of the buried F14 specimen was recorded at 0, 15, 30, and 60 d. After removal for photography, loose soil particles on the film surface were gently removed without strong washing or deliberate mechanical disruption to avoid artificially damaging the weakened structure. The macroscopic appearance was photographed under similar conditions, with attention to surface roughening, color change, edge fragmentation, cracking, loosening, perforation, and loss of structural continuity.

To supplement the original 0–60 d appearance-based observation, the representative F14 specimen that remained under the same indoor soil exposure conditions was additionally recorded after 124 d and then recovered for standardized endpoint photography. Loose adhering soil particles were gently removed by light manual dry cleaning without water rinsing, ultrasonic treatment, or deliberate mechanical disruption. Because tracked replicate specimens, individual initial dry masses, and intermediate-time residual samples were not retained in the original trial, no retrospective mass loss calculation or time-resolved deterioration analysis was performed.

Because this soil burial test was limited to macroscopic appearance observations, the results should be interpreted only as qualitative evidence of soil exposure-induced structural deterioration, rather than as a complete quantitative assessment of biodegradation. More systematic evaluation, including residual mass tracking, time-resolved recovered-sample characterization, and mineralization-related assessment, should be conducted in future work [43,44].

3. Results and Discussion

3.1. SEM Characterization and Surface Morphology Comparison

To provide morphological evidence for the incorporation of HNTs into the starch-coated cow dung-based substrate, SEM observations were performed for pristine HNTs, the uncoated substrate, the starch-coated control film, and the representative starch/HNT-coated film F14 (Figure 3).

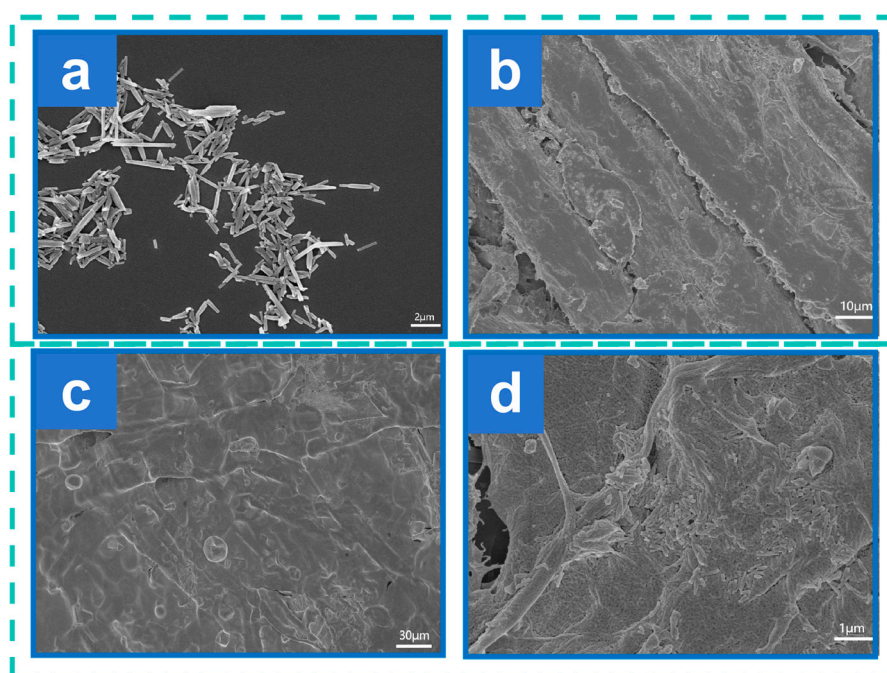


Figure 3. SEM micrographs of (a) pristine HNTs, (b) the uncoated cow dung-based substrate (F01), (c) the starch-coated control film (F02), and (d) the starch/HNT-coated composite film F14. The images were used to compare the HNT particle morphology, the original substrate surface, the starch-coated surface, and the HNT-containing composite coating.

As shown in Figure 3a, the pristine HNTs exhibited elongated tubular or rod-like morphologies, together with localized particle aggregation. This characteristic morphology provides a direct reference for identifying HNT-related features on the surface of the starch/HNT-coated composite film.

The uncoated cow dung-based substrate displayed a heterogeneous fibrous and lamellar surface morphology, with exposed fiber-rich regions and irregular surface grooves (Figure 3b). This morphology reflects the intrinsic structure of the cow dung pulp-containing cellulose substrate. After starch coating, the surface became comparatively more continuous and compact, and part of the exposed fibrous structure was covered by a film-like coating layer (Figure 3c). This indicates that the cationic starch coating partially filled surface irregularities and formed a covering layer over the substrate surface.

In contrast to the starch-coated control, the starch/HNT-coated F14 film showed additional rod-like particles and locally clustered domains on the coating surface (Figure

3d). These features were morphologically consistent with the pristine HNTs shown in Figure 3a and appeared to be attached to or partially embedded in the starch-containing surface layer. The observed local clustering also indicates that the HNT distribution was not completely uniform at the microscopic observation scale.

Overall, the SEM results provide morphological evidence that the starch coating modified the original fibrous substrate surface and that HNT-like tubular particles were introduced into the starch-containing surface coating of F14. However, SEM alone does not prove chemical bonding between starch and HNTs, nor does it demonstrate fully homogeneous nanoscale dispersion throughout the entire film. Therefore, these results are interpreted as morphological evidence of HNT incorporation into the surface coating rather than as direct chemical interaction evidence.

3.2. Measured Mechanical Response of Starch/HNT-Modified Films

To establish the original mechanical screening dataset, fifteen formulations were prepared and tested, including one unmodified substrate, two single-component controls, and twelve starch/HNT composite formulations. The formulation distribution and measured mechanical responses are shown in Figure 4, while the detailed results are summarized in Table 7. For each formulation, three parallel specimens were tested, and the results are expressed as mean $\pm$ standard deviation.

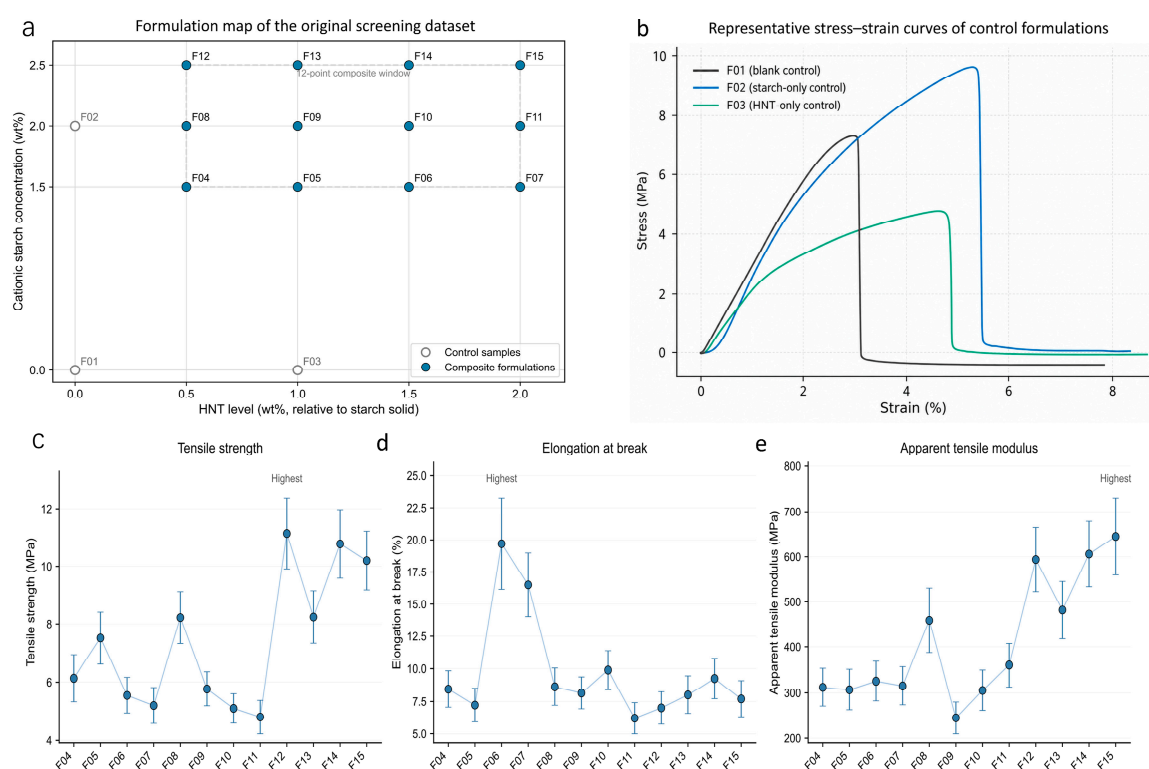


Figure 4. (a) Formulation distribution of the original screening samples; (b) representative stress-strain curves of the control samples; (c) tensile strength; (d) elongation at break; (e) apparent tensile modulus. Error bars represent standard deviations of three parallel specimens ($n = 3$).

The control results indicated that cationic starch improved the baseline mechanical response of the cow dung-based substrate. Compared with F01, the starch-only control F02 showed higher tensile strength and apparent tensile modulus. In contrast, the HNT-only control F03 did not improve either tensile strength or modulus under the present

coating conditions. These results indicate that the contribution of HNT should be evaluated within the starch-containing composite formulation window rather than as an isolated reinforcement treatment.

Within the starch/HNT composite window, the three mechanical indicators reached their highest values at different formulations. F12, containing 2.5 wt% starch and 0.5 wt% HNT, showed the highest tensile strength of 11.14 ± 1.23 MPa. F06, containing 1.5 wt% starch and 1.5 wt% HNT, exhibited the highest elongation at break of $19.70 \pm 3.55\%$. F15, containing 2.5 wt% starch and 2.0 wt% HNT, showed the highest apparent tensile modulus of 645.00 ± 85.14 MPa. Overall, higher starch content tended to favor tensile strength and apparent tensile modulus, whereas higher elongation at break was mainly observed in the lower-starch region with appropriate HNT addition. Neither tensile strength nor modulus increased monotonically with HNT level, suggesting that the effect of HNT depended on its matching relationship with the starch phase.

Because the formulations favorable for tensile strength, elongation at break, and apparent tensile modulus were not identical, the spatial distribution of the three mechanical responses within the composite formulation window was further examined in the following section.

Table 7. Mechanical properties of the original fifteen screening formulations used for mechanical balance analysis and model development.

Sample	Starch (wt%)	HNT (wt%)	Tensile Strength (MPa)	Elongation at Break (%)	Apparent Tensile Modulus (MPa)
F01	0	0	7.33 ± 0.81	7.84 ± 1.29	321.00 ± 38.52
F02	2.0	0	9.64 ± 0.96	8.32 ± 1.25	363.00 ± 47.92
F03	0	1.0	4.80 ± 0.62	8.67 ± 1.43	254.00 ± 33.53
F04	1.5	0.5	6.13 ± 0.80	8.45 ± 1.39	311.95 ± 41.18
F05	1.5	1.0	7.51 ± 0.90	7.22 ± 1.30	306.77 ± 44.17
F06	1.5	1.5	5.55 ± 0.61	19.70 ± 3.55	325.20 ± 42.93
F07	1.5	2.0	5.20 ± 0.62	16.50 ± 2.48	315.00 ± 41.58
F08	2.0	0.5	8.22 ± 0.90	8.63 ± 1.42	458.81 ± 71.57
F09	2.0	1.0	5.77 ± 0.58	8.15 ± 1.22	244.59 ± 35.22
F10	2.0	1.5	5.10 ± 0.51	9.89 ± 1.48	305.26 ± 43.96
F11	2.0	2.0	4.80 ± 0.58	6.20 ± 1.21	360.00 ± 47.52
F12	2.5	0.5	11.14 ± 1.23	7.00 ± 1.26	593.81 ± 71.26
F13	2.5	1.0	8.24 ± 0.91	8.01 ± 1.44	481.81 ± 63.60
F14	2.5	1.5	10.78 ± 1.19	9.25 ± 1.53	606.00 ± 72.72
F15	2.5	2.0	10.20 ± 1.02	7.70 ± 1.39	645.00 ± 85.14

Table note: Values are presented as mean $\pm$ standard deviation based on three parallel specimens ($n = 3$).

3.3. Spatial Mismatch of High Value Mechanical Regions Within the Composite Window

To further clarify the formulation-dependent distribution of the three mechanical properties and support subsequent formulation screening, the mean values of the twelve starch/HNT composite formulations were remapped into the two-dimensional formulation space defined by cationic starch content and HNT level, as shown in Figure 5. Compared with the sample code-based comparison in Figure 4, Figure 5 more directly shows whether the favorable regions of tensile strength, elongation at break, and apparent tensile modulus overlapped within the starch/HNT composite window. The corresponding standard deviations are listed in Table 7.

As shown in Figure 5a, the high value region of tensile strength was mainly observed at higher starch content. However, clear differences still appeared among HNT levels at the same starch level, indicating that the strength response was not determined solely by

starch content. This result suggests that HNT addition should be considered in relation to the starch phase when selecting strength-priority formulations, rather than being treated as a monotonic reinforcing factor.

In contrast, Figure 5b shows that the favorable region of elongation at break shifted away from the high strength region. Higher elongation was observed mainly at lower starch content with appropriate HNT addition, indicating that the formulation conditions favorable for deformation tolerance differed from those favorable for tensile resistance.

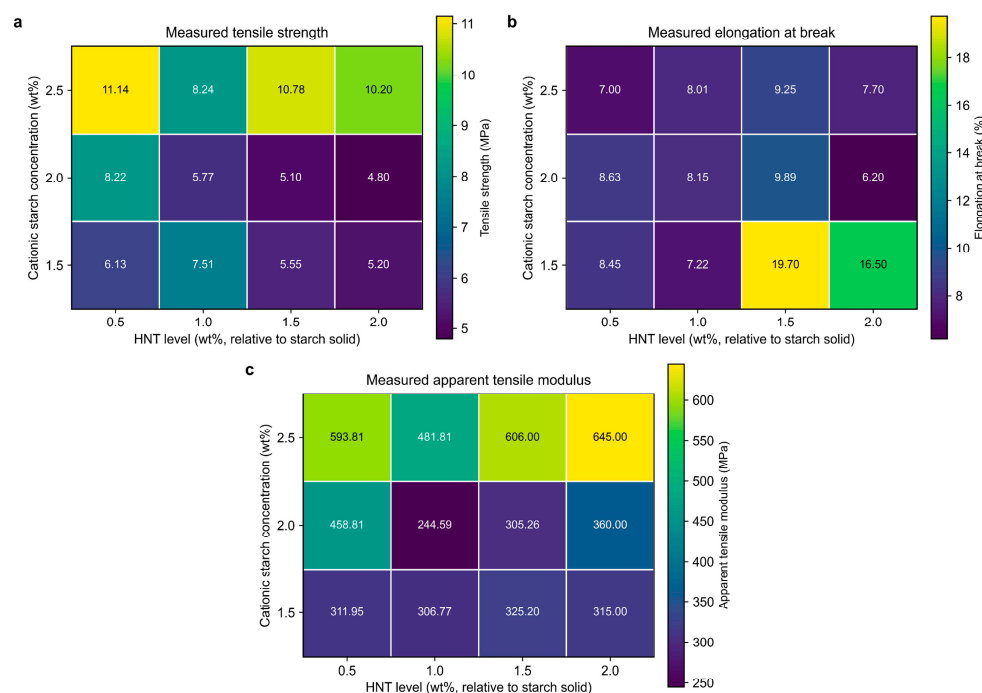


Figure 5. (a) Tensile strength; (b) elongation at break; (c) apparent tensile modulus. The maps were generated using the mean values of the twelve starch/HNT composite formulations. The corresponding standard deviations are listed in Table 7.

Figure 5c further shows that the apparent tensile modulus was mainly biased toward the high starch region, especially under relatively high HNT levels. This pattern indicates that the stiffness-related response was more favorable when higher starch content was combined with appropriate HNT addition. However, the modulus distribution still differed from the tensile strength and elongation distributions, indicating that stiffness-priority selection also requires separate consideration within the formulation window.

Overall, the spatial distributions in Figure 5 demonstrate that the high value regions of tensile strength, elongation at break, and apparent tensile modulus did not fully overlap. Tensile strength and apparent tensile modulus were more concentrated in the high starch region, whereas elongation at break was more favorable in a lower starch region with appropriate HNT addition. Therefore, formulation selection in this system should not be based on maximizing a single mechanical property. Instead, it should be treated as a multi-index mechanical balance problem involving strength, ductility, and stiffness. The interpretation in this section is based on mechanical response distributions, and more detailed structural characterization may further clarify the underlying mechanism in future work.

3.4. Data-Assisted Trend Mapping and Variable Contribution Analysis

3.4.1. LOOCV Performance of Data-Assisted Models

To examine whether the measured formulation-dependent mechanical responses could be organized into local response trends for candidate window screening, data-assisted trend mapping was performed using the original fifteen screening formulations. The control samples F01–F03 were included as boundary references, while F04–F15 described the starch/HNT composite formulation window. The relationship between measured and LOOCV-predicted values is shown in Figure 6, and the corresponding model performance is summarized in Table 8.

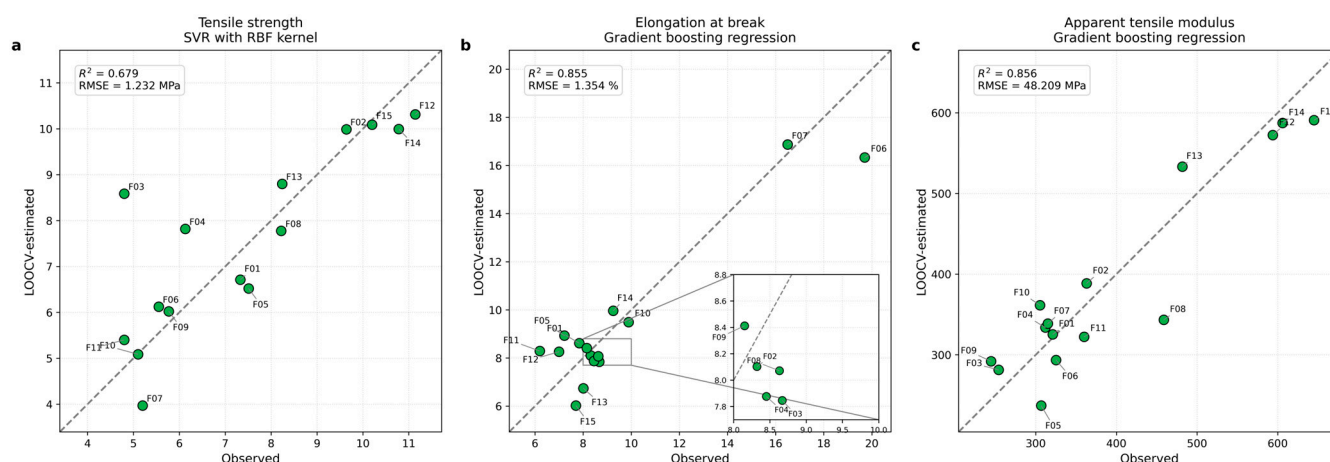


Figure 6. LOOCV prediction performance of data-assisted models for mechanical properties. (a) Tensile strength; (b) elongation at break; (c) apparent tensile modulus. The dashed line represents the ideal agreement between measured and predicted values.

The LOOCV results showed that the models captured the main local trends in the three mechanical indicators, although their trend-mapping reliability varied across target properties. The tensile strength model based on SVR with an RBF kernel gave an LOOCV R^2 of 0.679 and an RMSE of 1.232 MPa, indicating moderate trend-mapping ability rather than high accuracy prediction. The GBR models for elongation at break and apparent tensile modulus showed better LOOCV performance, with R^2 values of 0.855 and 0.856 and RMSE values of 1.354% and 48.209 MPa, respectively.

These results support the use of SVR and GBR as auxiliary tools for local response visualization and candidate region interpretation. However, because the dataset contained only fifteen tested formulations, the models were not used for extrapolative prediction or as independent evidence of an absolute optimum. Accordingly, the subsequent response maps were interpreted as decision support visualizations for identifying relative candidate regions within the tested formulation space.

Table 8. LOOCV performance of data-assisted trend-mapping models.

Target Property	Selected Model	LOOCV (R^2)	RMSE
Tensile strength	SVR with RBF kernel	0.679	1.232 MPa
Elongation at break	Gradient boosting regression	0.855	1.354%
Apparent tensile modulus	Gradient boosting regression	0.856	48.209 MPa

3.4.2. Model-Predicted Trend Maps Within the Composite Formulation Window

Based on the final models selected for each mechanical indicator, response maps were generated within the tested starch/HNT composite window, as shown in Figure 7. The display range was limited to starch contents of 1.5–2.5 wt% and HNT levels of 0.5–2.0

wt%, corresponding to the experimentally tested composite formulation space. Although F01–F03 were included in model training as boundary references, they were not shown as candidate points in the composite window maps because they did not contain both starch and HNT components.

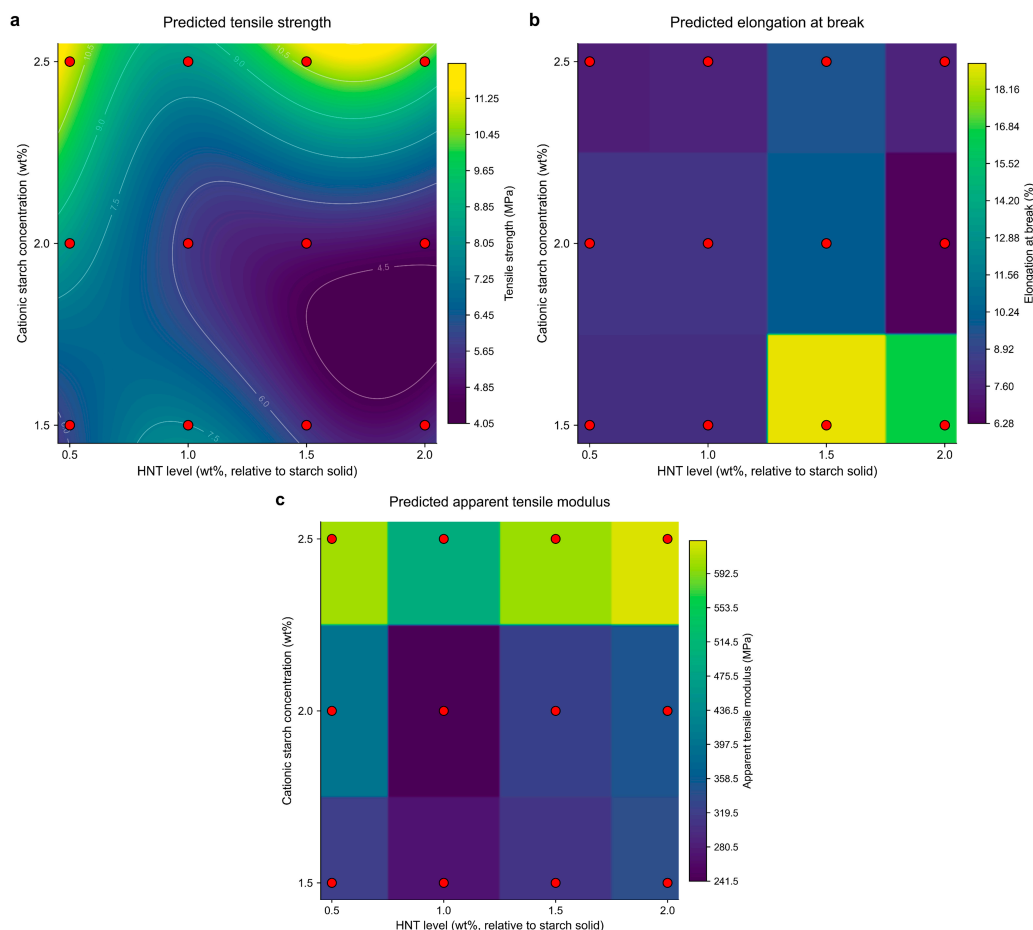


Figure 7. Model-predicted mechanical response maps within the starch/HNT composite window. (a) Tensile strength; (b) elongation at break; (c) apparent tensile modulus. The maps were generated only within the tested composite formulation range, and the red points indicate the measured starch/HNT composite samples.

The predicted maps were broadly consistent with the measured spatial distributions in Figure 5. The predicted high value region of tensile strength was mainly located near the higher starch content region, while the elongation-at-break map showed a shifted favorable region toward lower starch content with appropriate HNT addition. For apparent tensile modulus, the predicted high value region was mainly concentrated at higher starch levels and relatively high HNT levels. These patterns further indicated that tensile strength, elongation at break, and apparent tensile modulus responded differently to starch content and HNT level. This model-assisted mismatch provided the basis for the subsequent desirability-based consensus analysis, in which the separate mechanical response maps were integrated into a candidate window screening result.

Overall, the data-assisted maps provided a visual summary of local mechanical response trends within the tested composition range and helped identify relatively favorable regions for subsequent formulation screening. These maps should be interpreted alongside the measured data rather than as precise continuous predictions.

3.4.3. Relative Contribution of Starch Content and HNT Level

Permutation importance analysis was performed to describe the relative sensitivity of each mechanical property model to starch content and HNT level. The normalized contribution results are shown in Figure 8. This analysis reflects model sensitivity within the current dataset and was used to support formulation-variable interpretation, rather than to prove microstructural mechanisms or causal interactions.

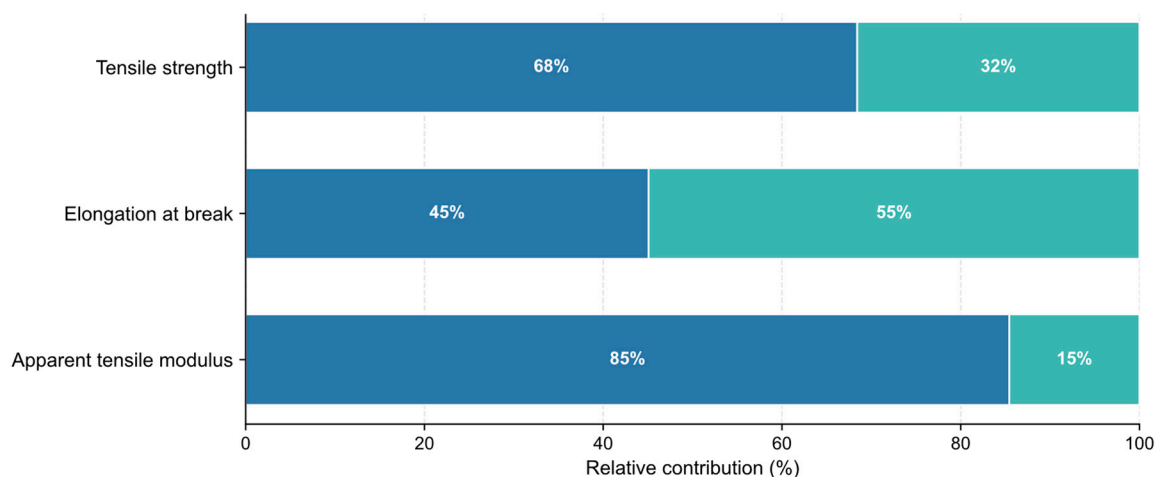


Figure 8. Relative contributions of starch content and HNT level to mechanical property prediction. Dark blue represents the relative contribution of cationic starch content, whereas light green represents the relative contribution of HNT level.

For tensile strength prediction, cationic starch content showed a higher contribution than HNT level, accounting for approximately 68% of the total normalized contribution. This result is consistent with the measured strength distribution, in which higher tensile strength values were mainly observed at the 2.5 wt% starch level. For elongation at break, the contribution of HNT level was slightly higher, accounting for approximately 55%, suggesting that HNT level played a more prominent role in regulating the local deformation response under lower starch conditions. For apparent tensile modulus, starch content showed the dominant contribution, accounting for approximately 85%, consistent with the high-modulus region observed at higher starch content.

Overall, the variable contribution analysis supports the performance-level interpretation that cationic starch was more closely related to strength and stiffness responses. In contrast, HNT level was more involved in local elongation regulation. Therefore, these contribution values should be interpreted as model-based evidence of sensitivity for screening-stage formulation analysis, rather than as direct proof of underlying structural mechanisms.

3.5. Mechanical Balance Ranking and Weighting Sensitivity Analysis

Because the high value regions of tensile strength, elongation at break, and apparent tensile modulus did not fully overlap, a single mechanical property was insufficient to identify the most favorable formulation. Therefore, a normalized mechanical balance score was used to compare the overall mechanical performance of the original fifteen screening formulations. The equal weight scheme was used as the baseline evaluation, while three alternative weighting schemes were used to examine whether the ranking was sensitive to different mechanical priorities.

As shown in Figure 9, with the equal weight baseline, F14 obtained the highest mechanical balance score of 0.691, followed by F15 and F12, with scores of 0.654 and 0.644,

respectively. Although F14 did not show the highest value in any single mechanical property, it combined relatively high tensile strength, moderate elongation at break, and high apparent tensile modulus. In contrast, F12 represented the strength-priority direction, while F15 represented the stiffness-priority direction. Therefore, F14 was identified as the most favorable mechanically balanced formulation with the neutral equal weight criterion.

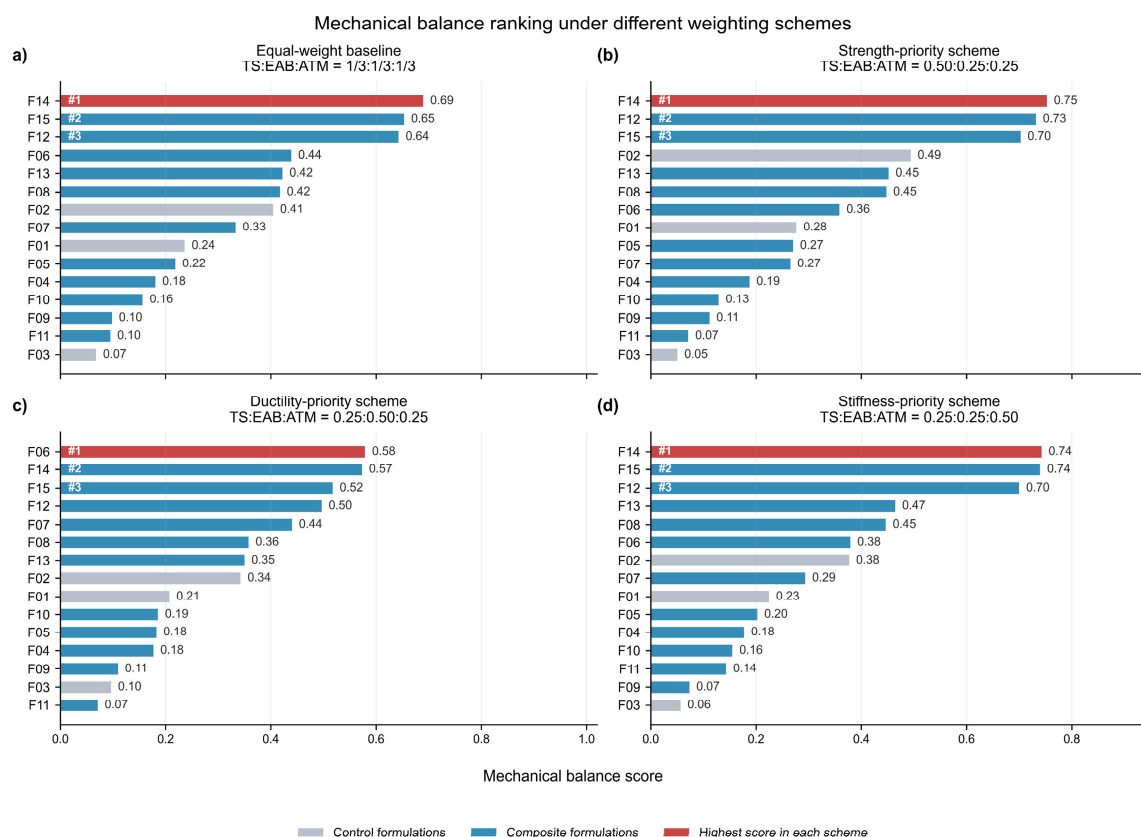


Figure 9. Mechanical balance score ranking under different weighting schemes. Red bars indicate the highest scoring formulation under each weighting scheme, gray bars indicate control samples, and blue bars indicate starch/HNT composite formulations. The labels “#1”, “#2”, and “#3” denote the first-, second-, and third-ranked formulations, respectively, under each weighting scheme.

The full weighting sensitivity results are listed in Table 9. Under the strength-priority scheme, F14 still ranked first, followed by F12 and F15. Under the ductility-priority scheme, F06 ranked first due to its much higher elongation at break, while F14 ranked second. Under the stiffness-priority scheme, F14 and F15 were nearly tied, with scores of 0.744 and 0.741, respectively. These results indicate that the ranking was not determined solely by the equal weight assumption. Instead, F14 remained the first- or second-ranked formulation across all tested weighting schemes.

Overall, the mechanical balance analysis demonstrates that the present formulation selection problem cannot be addressed by single-property maximization alone. F12, F06, and F15 represented favorable directions for tensile strength, ductility, and stiffness, respectively, whereas F14 showed the most stable ranking under different weighting assumptions. Thus, the role of the balance analysis was to distinguish a mechanically balanced candidate from the separate single-property optima within the tested sample set. Because this result was derived from discrete formulations, a desirability-based consensus analysis was then used to determine whether a neighboring model-assisted candidate region could be prioritized for independent testing.

Table 9. Mechanical balance scores and ranks under different weighting schemes.

Sample	Equal Weight Score/Rank	Strength-Priority Score/Rank	Ductility-Priority Score/Rank	Stiffness-Priority Score/Rank
F01	0.237/9	0.278/8	0.208/9	0.226/9
F02	0.405/7	0.495/4	0.343/8	0.378/7
F03	0.069/15	0.052/15	0.097/14	0.057/15
F04	0.182/11	0.189/11	0.178/12	0.178/11
F05	0.219/10	0.271/9	0.183/11	0.203/10
F06	0.440/4	0.359/7	0.580/1	0.380/6
F07	0.334/8	0.266/10	0.441/5	0.294/8
F08	0.418/6	0.448/6	0.359/6	0.447/5
F09	0.099/13	0.113/13	0.110/13	0.074/14
F10	0.157/12	0.130/12	0.186/10	0.156/12
F11	0.096/14	0.072/14	0.072/15	0.144/13
F12	0.644/3	0.733/2	0.498/4	0.701/3
F13	0.423/5	0.453/5	0.351/7	0.465/4
F14	0.691/1	0.754/1	0.574/2	0.744/1
F15	0.654/2	0.704/3	0.518/3	0.741/2

3.6. Desirability-Based Consensus High-Potential Window Identification

The measured mechanical balance ranking identified F14 as the most stable mechanically balanced formulation among the tested samples. However, this result was based on discrete experimental formulations. To bridge the gap between the discrete mechanical balance ranking and model-assisted formulation window prioritization, a desirability-based consensus analysis was conducted within the tested starch/HNT formulation space.

For each grid point, tensile strength, elongation at break, and apparent tensile modulus were converted into individual desirability values and then integrated into an overall desirability score under four weighting schemes: equal weight, strength-priority, ductility-priority, and stiffness-priority. Under each weighting scheme, grid points satisfying ($D_w \geq 0.85 D_{w,max}$) were considered high-potential points. A grid point was further defined as belonging to the consensus high-potential window when it satisfied this threshold under at least three of the four weighting schemes.

As shown in Figure 10, the overall desirability distribution was not uniform within the tested formulation space. The highest desirability region appeared near the high starch/intermediate HNT region. The largest continuous consensus high-potential window was identified at 2.300–2.500 wt% starch and 1.251–1.747 wt% HNT, which is described approximately as 2.30–2.50 wt% starch and 1.25–1.75 wt% HNT in the following discussion. This region was close to F14, which corresponded to 2.5 wt% starch and 1.5 wt% HNT. This consistency suggests that F14 was not only the most stable mechanically balanced formulation among the tested samples, but also located near a model-assisted high-potential region that remained favorable across different mechanical priorities.

It should be emphasized that the consensus window should not be interpreted as an absolute optimum predicted by the model. Rather, it represented a model-assisted priority region within the present screening-stage study. The desirability-based consensus analysis therefore converted separate mechanical response maps into experimentally testable candidate compositions. To examine whether this prioritization provided useful guidance beyond the original screening dataset, four previously untested formulations were selected from the frozen consensus window, independently prepared, and tested, as reported in Section 3.7.

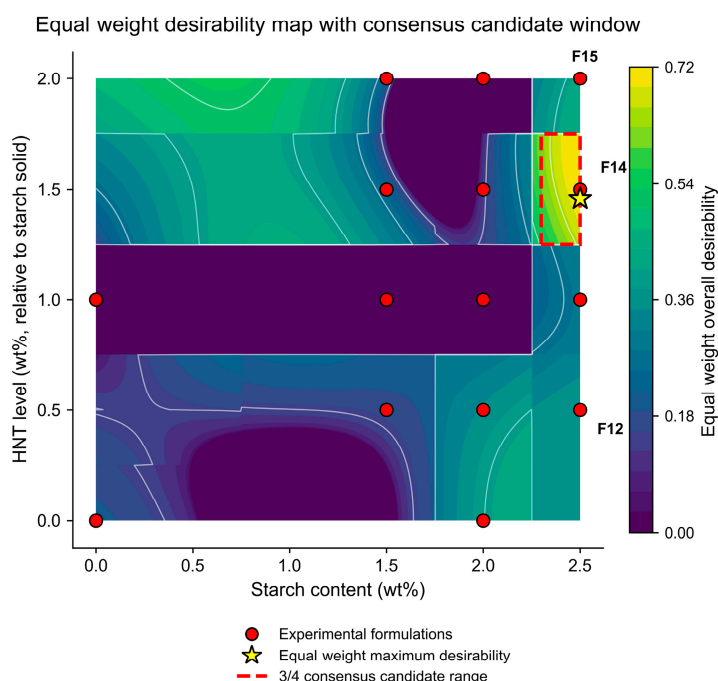


Figure 10. Desirability-based consensus high-potential window within the starch/HNT formulation space. The colored background represents the overall desirability distribution. Red points indicate the tested formulations, the yellow star indicates the maximum desirability point, and the red dashed region indicates the consensus high-potential window supported by at least three of the four weighting schemes.

3.7. Independent Experimental Validation of Model-Guided Candidate Formulations

To examine whether the model-defined consensus candidate region provided experimentally meaningful guidance, four previously untested formulations, V1–V4, were selected only after the original models, desirability reference bounds, weighting schemes, and consensus thresholds had been fixed. The validation samples were then independently prepared and tested and were not included in model training, LOOCV evaluation, hyperparameter selection, or desirability window construction. The prediction–experiment comparison in Table 10 therefore provides an independent assessment of whether the frozen workflow could prioritize candidate compositions within the investigated formulation range.

Table 10. Independent experimental validation of four previously untested formulations selected from the consensus candidate region.

Formulation	Starch (wt%)	HNT Level (wt%)	Tensile Strength, Predicted (MPa)	Tensile Strength, Experimental (MPa)	Elongation at Break, Predicted (%)	Elongation at Break, Experimental (%)	Apparent Tensile Modulus, Predicted (MPa)	Apparent Tensile Modulus, Experimental (MPa)
V1	2.5	1.6	11.17	10.79 ± 1.08	9.59	8.97 ± 1.07	600.96	610.40 ± 62.55
V2	2.5	1.3	9.56	9.72 ± 1.02	9.59	8.89 ± 1.30	600.96	569.83 ± 60.15
V3	2.4	1.5	9.40	9.62 ± 1.02	9.59	9.38 ± 1.28	600.96	549.73 ± 65.05
V4	2.4	1.7	9.84	9.42 ± 1.04	9.59	8.61 ± 1.20	600.96	564.67 ± 65.10

Table note: V1–V4 were selected from the frozen model-defined consensus candidate region and were not included in model training, LOOCV evaluation, model selection, or desirability window construction. Experimental values are reported as mean ± standard deviation ($n = 3$).

Overall, the predicted values showed good agreement with the experimental results within the selected candidate region. Across all twelve prediction–experiment comparisons, the frozen model predictions fell within the corresponding experimental mean $\pm$ standard deviation intervals. Across the four validation formulations, the mean absolute percentage errors were 2.96% for tensile strength, 7.03% for elongation at break, and 5.69% for apparent tensile modulus. In particular, V1, containing 2.5 wt% starch and 1.6 wt% HNT, exhibited experimentally measured values of 10.79 ± 1.08 MPa in tensile strength, $8.97 \pm 1.07\%$ in elongation at break, and 610.40 ± 62.55 MPa in apparent tensile modulus, compared with predicted values of 11.17 MPa, 9.59%, and 600.96 MPa, respectively. The results support the practical consistency of the frozen models for prioritizing candidate compositions within the investigated formulation range. However, because the elongation and modulus models showed locally plateau-like predictions in this narrow region, the present validation should be interpreted as support for local candidate region prioritization rather than evidence of global predictive accuracy or a unique optimum formulation.

3.8. Preliminary Indoor Soil Burial Appearance Evolution and Endpoint Macroscopic Observation of F14

Based on the mechanical balance ranking, the weighting sensitivity analysis, and its location near the consensus high-potential window, F14 was selected as the representative favorable formulation for preliminary indoor soil burial observation. This section focused on the time-dependent evolution of the selected sample's macroscopic appearance under soil contact conditions, rather than on quantitative biodegradation kinetics. The purpose was to examine whether the mechanically favorable formulation could maintain basic covering continuity during the early burial stage while showing progressive structural deterioration during longer exposure.

As shown in Figure 11a–d, the F14 sample showed an intact film layer with a relatively uniform surface and a clear boundary at 0 d, indicating sufficient initial structural continuity before burial. After 15 d, the sample still maintained overall covering continuity, although slight surface roughening and color changes began to appear. This suggests that the film did not undergo rapid early-stage collapse under the present soil contact conditions.

After 30 d of burial, more visible surface roughening, local loosening, and edge damage were observed. The film boundary became less regular, and the surface texture became more heterogeneous. By 60 d, edge fragmentation, local structural loosening, increased surface defects, and partial loss of film continuity became more obvious. The observed appearance evolution indicates a staged pattern in which the representative favorable formulation maintained basic covering continuity during the early burial period while gradually entering a progressive deterioration phase.

For biodegradable agricultural covering materials, a practical target is to balance early service stability with later-stage structural weakening, rather than to maximize durability or accelerate structural failure. Similar stage-dependent changes, including surface roughening, embrittlement, fragmentation, and gradual loss of film integrity under soil contact or field conditions, have also been reported for biodegradable mulch materials [43–45]. Therefore, the soil burial observation of F14 is consistent with the expected application-oriented requirement that the film should retain short-term covering continuity while gradually losing structural integrity during prolonged soil exposure.

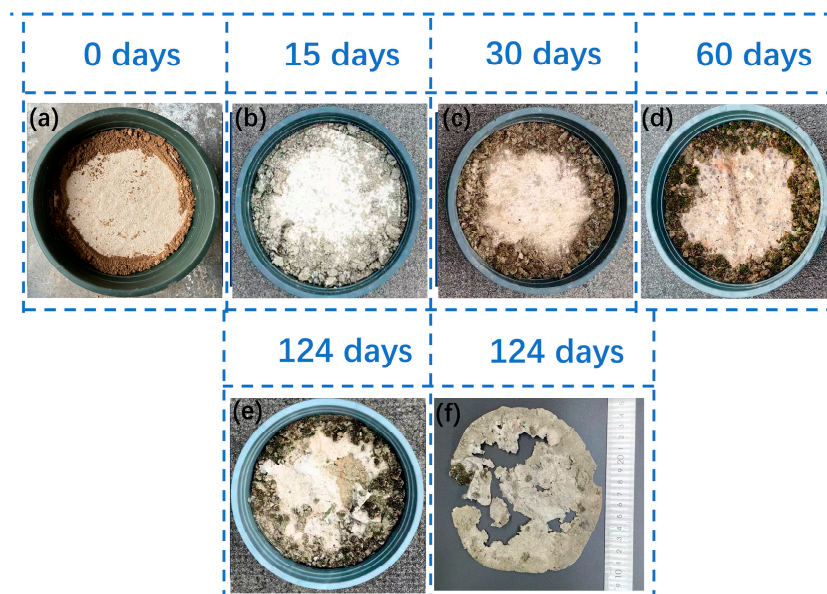


Figure 11. Macroscopic appearance evolution of F14 during the preliminary indoor soil burial observation at (a) 0 d, (b) 15 d, (c) 30 d, (d) 60 d, and (e) 124 d under the same indoor soil exposure conditions. (f) Standardized photograph of the recovered residual F14 specimen after 124 d of soil exposure. The 124 d endpoint images were included as supplementary long-term macroscopic evidence of structural deterioration rather than as a quantitative biodegradation rate assessment. The initial soil burial specimen was a circular F14 film with a diameter of approximately 15 cm.

To provide additional long-term endpoint evidence, the F14 specimen remaining under the same indoor soil exposure conditions was recorded after 124 d and then recovered for standardized photography (Figure 11e,f). The recovered specimen no longer retained its original geometrical integrity and showed pronounced perforation, irregular edge recession, local fragmentation, and discontinuity of the residual film network. This endpoint observation further supports the qualitative interpretation that prolonged soil exposure induced progressive macroscopic structural deterioration of the film.

Nevertheless, this section should be interpreted only as a qualitative observation of macroscopic structural deterioration. Because individual initial dry masses, tracked replicate specimens, and samples recovered at intermediate time points were not available from the original trial, the present study did not perform retrospective mass loss calculation, degradation rate analysis, or mineralization assessment. More systematic long-term soil burial tests with residual mass tracking and microstructural/chemical characterization will be conducted in future work.

3.9. Application Positioning and Future Perspectives

To position the present material within a broader application context, the tensile properties of the mechanically balanced formulation F14 were compared with representative biodegradable agricultural covering films and a commercial packaging/laminating film reported in the literature (Table 11). F14 exhibited a tensile strength of 10.78 ± 1.19 MPa and an elongation at break of $9.25 \pm 1.53\%$. Its tensile strength was higher than that reported for a PBAT/PLA-PVA-PDA biodegradable weed-control mulch film (7.9 MPa) and was close to that of a PBAT/PLA-PVA-PAA mulch film (10.2 MPa) [46]. However, both PBAT/PLA-based films exhibited substantially higher elongation at break, reflecting the greater ductility of continuous polyester-based matrices. In contrast, a multiply cross-linked cellulosic paper mulch film reached a higher dry tensile strength of 17 MPa after wet strength and hydrophobic treatments, whereas its wet tensile strength was reported

as 3 MPa [17]. These comparisons indicate that the present starch/HNT-modified cow dung-based film lies within a practically relevant tensile strength range for biodegradable agricultural covering materials, although its strength–ductility profile remains different from those of continuous polymer-based or strongly cross-linked film systems.

Table 11. Tensile properties of F14 and representative biodegradable agricultural covering, packaging, and laminating films reported in the literature.

Film System	Main Application	Tensile Strength (MPa)	Elongation at Break (%)	Reference
F14 in the present study	Agricultural covering film	10.78 ± 1.19	9.25 ± 1.53	Present study
PBAT/PLA-PVA-PDA film	Biodegradable weed-control mulch film	7.9	343.2	[46]
PBAT/PLA-PVA-PAA film	Biodegradable weed-control mulch film	10.2	509.3	[46]
Cross-linked cellulosic paper mulch film	Waterproof biodegradable mulch film	17.0 (dry); 3.0 (wet)	NR	[17]
Heat-sealable BOPP film	Packaging and laminating film	130–150 (MD); 290 (TD)	180–220 (MD); 60 (TD)	[47]

Table note: MD, machine direction; TD, transverse direction; NR, not reported. The values were collected from independent studies and technical data sheets and are presented only for contextual comparison. Direct quantitative comparison should be interpreted cautiously, because the film composition, thickness, conditioning conditions, specimen geometry, crosshead speed, processing route, orientation history, and intended application differ among studies.

Packaging and laminating films were considered as a secondary application context. Compared with highly oriented commercial BOPP films, the present cow dung pulp-containing fiber network film exhibits substantially lower tensile strength and elongation at break [47]. This difference is expected, because BOPP films are continuous polymer materials produced through controlled extrusion and biaxial orientation and are designed to meet demanding requirements related to mechanical durability, barrier performance, heat sealing, transparency, printability, and migration control. Therefore, the present film is not positioned as a direct replacement for high-performance packaging or laminating substrates. Instead, its potential value lies in the use of a cow dung pulp-containing cellulose substrate and a water-based starch/HNT coating process, which may support agricultural waste valorization and reduce reliance on virgin petrochemical feedstocks. These potential circular economy benefits should not be interpreted as having demonstrated overall environmental superiority or faster biodegradation than other packaging films, because such conclusions would require standardized comparative biodegradation testing and life-cycle assessment.

Future work may extend the present material toward multifunctional agricultural covering applications. The hollow lumen and surface adsorption capacity of HNTs could be explored for nutrient loading before coating, followed by evaluation of nutrient release kinetics, soil leaching, crop response, and the mechanical stability of the film during nutrient release [48]. In addition, HNTs could serve as carriers for environmentally compatible antimicrobial or antifungal agents, such as essential oils or other active compounds, to develop active agricultural covering films [49]. Such studies should further assess active agent loading, release behavior, functional efficacy, soil compatibility, ecological effects, wet-state strength, tear resistance, puncture resistance, weathering stability, and field-scale crop performance.

4. Conclusions

In this study, starch/HNT-modified cow dung-based biodegradable films were prepared using a unified brush-coating process, and their surface morphology, mechanical response, mechanical balance ranking, model-assisted trend distribution, candidate window identification, independent validation, and preliminary soil burial appearance evolution were investigated. SEM observations of pristine HNTs, the uncoated substrate, the starch-coated control, and the representative starch/HNT-coated film provided morphological evidence consistent with starch coating formation and the physical incorporation of HNTs into the surface coating layer. The high value regions of tensile strength, elongation at break, and apparent tensile modulus did not fully overlap: F12, F06, and F15 showed the highest values for these three indicators, respectively. Based on the mechanical balance score and weighting sensitivity analysis, F14 was identified as the most stable mechanically balanced formulation in the tested sample set.

Using the original fifteen screening formulations, SVR and GBR models were applied as auxiliary tools for bounded local trend mapping within the investigated starch/HNT composition range. The desirability-based consensus analysis identified a high-potential window at approximately 2.30–2.50 wt% starch and 1.25–1.75 wt% HNT, close to F14. Four previously untested formulations selected from the frozen consensus region were then independently prepared and tested. The agreement between the predicted and measured mechanical properties supported the practical consistency of the workflow for prioritizing candidate compositions within the investigated formulation range, while the validation results were interpreted as support for local candidate region prioritization rather than proof of global predictive accuracy or a unique optimum formulation.

Rather than replacing experimental formulation design or identifying a universal optimum, the proposed workflow integrates experimental screening, multi-scenario mechanical balance evaluation, bounded local trend mapping, consensus candidate window identification, and independent experimental assessment. Preliminary indoor soil burial observation of F14 showed early covering continuity followed by progressive surface roughening, edge fragmentation, perforation, and loss of structural continuity; the recovered residual specimen after 124 d further indicated pronounced long-term macroscopic deterioration. These observations were interpreted only as qualitative evidence of soil exposure-induced structural deterioration and not as a quantitative biodegradation rate or mineralization assessment. Overall, this integrated workflow provides a practical decision support route for prioritizing subsequent formulation refinement of agricultural waste-based biodegradable covering materials.

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