

Blend-Ratio-Dependent Tensile Tradeoffs in Sodium-Periodate-Treated High-Amylose Starch/Poly(vinyl alcohol) Films

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Abstract

High-amylose starch/poly(vinyl alcohol) (HAMS/PVA) blends are attractive as renewable-content film materials, but their tensile response depends strongly on starch chemistry, blend ratio, processing, and moisture history. This study compared sodium-periodate-treated HAMS/PVA mass ratios of 1:1 (S1P1), 1:2 (S1P2), and 2:1 (S2P1) with an untreated HAMS/PVA 1:2 control (H1P2) and neat PVA. A 4% (w/v) HAMS dispersion was treated with 4.8 g sodium periodate per 4.0 g starch at 34 °C for 1 h under light-shielded conditions and dialyzed for 72 h. No plasticizer, acid catalyst, filler, or other processing aid was added. Films were solution-cast and tested as 10 mm wide strips at an initial grip separation of 100 mm and a crosshead speed of 10 mm min⁻¹. Using the confirmed centimeter-scale thickness records converted to millimeters, nominal tensile strength and crosshead-derived elongation at break were recalculated from the machine reports. H1P2 had the highest descriptive strength (5.82 ± 0.92 MPa) but fractured at $2.77 \pm 0.21\%$ elongation. At the same 1:2 ratio, periodate treatment reduced strength to 1.51 ± 0.09 MPa while increasing elongation to $27.37 \pm 6.71\%$. Increasing the treated-starch fraction to 2:1 raised strength to 4.24 ± 0.73 MPa, 14.0% above neat PVA (3.72 ± 0.09 MPa), but its elongation remained much lower at $18.12 \pm 12.57\%$ compared with $128.24 \pm 13.89\%$ for PVA. The data therefore identify a composition-dependent tradeoff between strength and extensibility rather than a universal optimum. Periodate cleavage can introduce aldehyde-type functionality and may alter hydrogen bonding, chain packing, and aldehyde-hydroxyl reactions, but covalent crosslinking was not directly measured. The results support further mechanistic and packaging-performance testing of treated HAMS/PVA blends. They do not establish food-contact suitability, barrier performance, or biodegradability.

Keywords

Sodium Periodate; High-amylose Starch; Poly(Vinyl Alcohol); Solution Casting; Tensile Strength; Elongation at Break; Technical Replication.

1. Introduction

Petroleum-based polymers remain dominant in packaging because they are inexpensive, lightweight, and easy to process. The same durability that supports their use also contributes to their long-term accumulation when collection and recycling are incomplete [1,2]. This has increased interest in films containing a greater proportion of renewable raw materials. A viable alternative must still tolerate handling and deformation during use, so environmental motivation alone is not sufficient.

Starch is abundant, renewable, and capable of forming continuous films after gelatinization. Starch-rich films are nevertheless sensitive to moisture and may become brittle during drying or storage [1-6]. PVA is commonly blended with starch because it forms coherent films and contains hydroxyl

groups that can interact with the polysaccharide matrix. The properties of these blends depend on composition, PVA grade, water content, drying conditions, and specimen history. Conclusions obtained for one starch/PVA system therefore cannot be transferred directly to another.

Chemical treatment provides one approach to changing these interactions. Sodium periodate cleaves the bond between C2 and C3 at vicinal diol sites in a glucopyranose unit and can generate aldehyde-type functionality [15]. The treatment may alter hydrogen bonding, chain packing, molecular weight, and the possibility of reactions between aldehyde and hydroxyl groups. Previous studies provide a useful mechanistic basis, but their starch types and processing conditions differ from those used here. Direct comparison is needed before a particular tensile response can be assigned to covalent crosslinking.

The present study evaluates three sodium-periodate-treated high-amylose starch/PVA ratios and compares them with an untreated 1:2 blend and neat PVA. The analysis focuses on nominal tensile strength and crosshead-derived elongation at break after correction of the specimen dimensions recorded in the machine files. The objectives are to determine how blend ratio and starch treatment alter the balance between strength and extensibility, and to identify which observations require further chemical or structural verification. This work is a mechanical screening study rather than a final demonstration of packaging suitability.

2. Relevant Literature Review

This focused narrative review synthesizes the papers supplied for the present study. Full texts were accessed through the Beijing University of Chemical Technology library system. The review is not presented as a systematic search because no preregistered database strategy or formal study-selection protocol was applied. The emphasis is placed on studies that clarify starch-film limitations, starch/PVA interactions, oxidation chemistry, reinforcement, water response, degradation, and mechanical measurement.

2.1 Starch Films and Packaging Constraints

Starch is attractive as a film-forming material because it is renewable, widely available, and able to produce a continuous matrix after gelatinization. Its hydroxyl-rich structure also creates a persistent limitation. Extensive hydrogen bonding supports film formation but gives the material a strong affinity for water. Starch films can therefore show high moisture sensitivity, causing limited dimensional stability, and pronounced changes during storage [1-6]. Amylose content is important, but botanical source, chain-length distribution, plasticization, casting conditions, thickness, and humidity must be considered at the same time.

Retrogradation further complicates mechanical performance. After gelatinization and drying, starch chains can reassociate into more ordered domains. This process can increase stiffness while decreasing elongation, and its rate depends on temperature and water content [1,2]. The reviews by Lauer and Smith, Bangar et al., Jayarathna et al., Lin et al., and Li et al. consequently describe physical treatment, chemical modification, polymer blending, and reinforcement as complementary rather than interchangeable strategies [1-5]. Vieira et al. reached a similar conclusion for hydrophobicity strategies. Esterification, crosslinking, waxes, oils, and fibers can improve selected water responses, but excessive reaction or poor dispersion can weaken film formation and flexibility [6].

Processing can produce changes comparable with those caused by composition. Wu et al. used response-surface optimization for a starch and fiber packaging material containing composite plasticizers [7]. Tensile strength increased by 12.2% under the optimized forming conditions. That thermally formed system differs from the aqueous films studied here, but it demonstrates why processing temperature, time, and solids content cannot be separated from material identity. A formulation should therefore be evaluated under the exact conditions used to produce it.

2.2 Starch/PVA Blend Formation and Mechanical Behavior

PVA is frequently combined with starch because it forms coherent films and presents hydroxyl groups that can associate with polysaccharides. These shared polar groups permit hydrogen bonding across the blend, although they also make both components responsive to water. Compatibility is not a simple yes-or-no property. Molecular association, phase continuity, crystallinity, and chain mobility vary with the starch source, PVA molecular characteristics, blend ratio, plasticizer, and drying conditions [8-13,16,25].

Gómez-Aldapa et al. studied potato-starch films containing up to 60 wt% PVA [8]. PVA improved tensile behavior and the water-vapor barrier relative to pure starch, while also increasing water adsorption. Cano et al. followed pea-starch/PVA films during five weeks of storage at 25 °C and 53% relative humidity [9]. Pure starch films became stronger and less stretchable as they aged, while PVA remained comparatively stable. The blends were partially miscible and showed lower water sensitivity and smaller storage-related changes than starch alone. These studies show that PVA can improve continuity and aging stability without making the blend fully homogeneous or hydrophobic.

Abramowska et al. examined glycerol-plasticized corn-starch/PVA films across the full composition range [10]. Starch-rich films were comparatively stiff and PVA-rich films were more flexible, but tensile strength passed through a minimum at intermediate compositions. Irradiation reduced hydrophilicity while also reducing flexibility. The response was attributed mainly to degradation, with possible crosslinking occurring at the same time. Ray et al. also found composition-dependent changes when starch/PVA films were reinforced with clay or crosslinked with epichlorohydrin [12]. These nonlinear responses caution against treating increasing PVA or increasing crosslink density as universally beneficial.

Structural studies explain part of this behavior. Popescu et al. observed spectroscopic evidence of hydrogen bonding in PVA/starch films and found that PVA crystallinity decreased as starch content increased [11]. Cellulose nanocrystals changed crystallinity and surface roughness further. Yao et al. showed that PVA polymerization and saponification levels also matter [13]. Their best hydroxypropyl- or octenylsuccinate-starch blends combined high tensile strength and elongation, but those modified starches and PVA grades differ from the materials used here. The numerical values are therefore useful as formulation-specific examples rather than direct benchmarks.

2.3 Oxidation Pathways and Periodate-treated Starch

Oxidized starch is not a single chemical category. Different oxidants act at different positions and generate products with different reactivity. Yang et al. used potassium permanganate in sulfuric acid to introduce mainly C6 carboxyl functionality into field-pea starch [14]. Blending this material with PVA and exfoliated alpha-zirconium phosphate improved tensile strength and reduced moisture uptake at a moderate filler loading. Larger filler contents caused aggregation and property deterioration. This work demonstrates the value of carboxyl-forming oxidation, but it does not establish the mechanism of periodate treatment.

Periodate follows a distinct pathway. It reacts at the vicinal hydroxyl groups on C2 and C3 of an anhydroglucose unit, cleaves the carbon-carbon bond, and produces ring-opened aldehyde-type sites [15]. In water, the carbonyl groups may be hydrated or incorporated into intra- and intermolecular hemiacetal structures. They can also react with PVA hydroxyl groups when the reaction and drying conditions are favorable. Periodate treatment can therefore change bonding, but it can also disrupt ordered packing and reduce molecular weight. These competing effects may produce either strengthening or softening.

Jia et al. provide the closest experimental precedent [15]. They treated a 4 wt% paste of hydroxypropyl tapioca starch with sodium periodate for 1 h away from light, dialyzed the material for three days, and homogenized it at high pressure. Iodometric analysis quantified aldehyde content and infrared spectroscopy detected a carbonyl band. The treated starch was blended with PVA at several ratios, acidified with dilute hydrochloric acid, and dried at 45 °C. The resulting films retained

wet strength and resisted rapid dissolution. The authors attributed the improved water stability to hemiacetal and acetal bonding, supported by chemical analysis, microscopy, swelling, immersion, and wet tensile tests.

That study establishes a credible mechanism under its own conditions, but it also defines the evidence needed to transfer the claim. The present films used high-amylose starch, no acid catalyst, no external plasticizer, and room-temperature drying. Aldehyde content, molecular weight, spectroscopy, swelling, and gel fraction were not measured. Stable acetal crosslinking therefore cannot be assumed. The defensible interpretation is that sodium periodate altered the starch and shifted its mechanical response. Hydrogen bonding, carbonyl hydration, hemiacetal equilibria, ring opening, chain scission, crystallinity, and retained moisture remain possible contributors.

2.4 Reinforcement and Interfacial Design

Nanofillers and reinforcing phases can improve starch-based films when they are dispersed well and interact with the matrix. At low loading, a high-aspect-ratio filler can transfer stress or create a tortuous diffusion path. At excessive loading, aggregation can introduce defects [11,14,17-20]. Garavand et al. added chitosan nanoparticles to a 60:40 PVA/starch matrix [17]. At 5% loading, tensile strength increased from about 35 to 47 MPa and water-vapor permeability decreased, while elongation and transparency declined. The same modification also introduced antimicrobial activity. The result illustrates a recurring tradeoff between strength, flexibility, optical behavior, and added function.

Dong et al. reported large stiffness and barrier gains after adding MXene nanoplatelets to starch films [18]. A 10 wt% loading increased tensile strength from 10 to 19 MPa and reduced water-vapor and oxygen permeability. Muñoz-Gimena et al. used starch nanocrystals from avocado-seed starch and found that 1% loading increased modulus and reduced water-vapor permeability, while higher loading promoted aggregation [19]. Ma et al. observed the same optimum-loading pattern for carboxylated silica in thermoplastic starch [20]. At 2 wt% modified silica, tensile and impact strength increased strongly. Higher loading increased brittleness and reduced the benefit.

These systems are not direct comparators for an unfilled HAMS/PVA film because each introduces a new phase and a new interface. Their shared contribution is a design principle. Reinforcement depends on dispersion, interfacial chemistry, and loading rather than the presence of a filler alone. The unfilled polymer matrix should therefore be evaluated first so the effects of starch treatment and blend ratio can be separated from later reinforcement strategies.

2.5 Water Resistance and Barrier Performance

Water resistance is not a single property. Water-vapor permeability, equilibrium moisture content, liquid-water uptake, swelling, dissolution, contact angle, and wet tensile strength describe different processes [1,2,6,8,9,13,15-18]. A dense film may slow vapor transport while still absorbing water during immersion. PVA improved the water-vapor barrier but increased water adsorption in the potato-starch system of Gómez-Aldapa et al. [8]. Cano et al. found that PVA helped preserve the low oxygen permeability of pea-starch films during aging [9]. Yao et al. showed that PVA saponification and starch substitution changed swelling, dissolution, and wet strength [13].

Jia et al. demonstrated water stability only after producing and verifying an aldehyde-containing network under acidified and heated conditions [15]. The chitosan, MXene, starch-nanocrystal, and silica studies improved selected water or gas-barrier measures through stronger interfacial association and more tortuous diffusion paths [17-20]. None of those results establishes the barrier performance of the present films. Dry tensile data are only an initial screen. Water-vapor and oxygen transmission, wet strength, sealing, optical properties, migration, and controlled-humidity storage must be tested before a packaging application can be supported.

2.6 Degradation, Dissolution, and Marine Behavior

Biodegradation, disintegration, dissolution, and mineralization describe different processes. Disintegration is loss of physical integrity. Dissolution transfers chains or fragments into a liquid. Biodegradation involves biological conversion, while complete mineralization requires conversion to final products such as carbon dioxide, water, biomass, and inorganic residues. Visual disappearance or mass loss alone does not establish mineralization [21].

Kliem et al. reviewed polymer degradation in compost, soil, sewage sludge, freshwater, seawater, and landfill environments [21]. Composting generally provided favorable conditions, while freshwater and seawater often produced slower biological degradation. Polymer composition, crystallinity, geometry, additives, and environmental conditions were reported inconsistently across the literature. Wicaksono et al. found 74% mass loss after burying a commercial cassava-starch bioplastic in compost soil for 120 days, compared with 3% for oxo-LDPE [22]. That result supports faster deterioration under the tested soil conditions, but it does not quantify mineralization or predict every starch formulation.

Marine-response studies further demonstrate the need for precise terminology. Jia et al. designed a grafted-starch/PVP film that was stable in deionized water but dissolved in artificial seawater when bicarbonate disrupted its hydrogen-bond network [23]. Soni et al. combined oxidized cellulose nanofibers with cationic starch to form a strong ionic complex [24]. Ionic screening in artificial seawater reduced wet strength and caused disintegration, while a neat oxidized-nanofiber film remained more stable. These were designed dissolution or disintegration responses, not proof of rapid marine mineralization. PVA degradation also depends on molecular weight, hydrolysis, crystallinity, and microbial conditions [16,21,25].

2.7 Evidence Synthesis and Research Gap

Table 1. Evidence map for the supplied literature and its relevance to the present study.

Theme	References	Main contribution
Starch-film foundations	1-7	Moisture sensitivity, retrogradation, processing dependence, modification strategies, and packaging requirements
Starch/PVA blends	8-13, 16, 25	Hydrogen bonding, partial miscibility, PVA grade, ratio, aging, crystallinity, and nonlinear mechanical response
Oxidation chemistry	14, 15	Difference between C6 carboxyl oxidation and periodate cleavage at the C2-C3 vicinal diol
Reinforcement	11, 14, 17-20	Dispersion-dependent changes in strength, elongation, permeability, optical behavior, and antimicrobial function
Water and barrier response	6, 8, 9, 13, 15, 17-20	Distinction among adsorption, vapor permeability, swelling, dissolution, wet strength, and contact angle
Environmental behavior	21-25	Distinction among biodegradation, disintegration, dissolution, mass loss, and mineralization
Characterization	26, 28, 29	Need for combined chemical identification and direct, configuration-aware strain measurement

The supplied literature establishes that PVA blending can improve continuity and storage stability, modified starch can change interfacial association, and periodate treatment can introduce aldehyde functionality capable of further reaction. It also shows that every strategy creates tradeoffs in flexibility, moisture response, transparency, or processability. Guan and Yan recommend combined chemical, thermal, and molecular methods for identifying modified starch plastics [26]. Mechanical

metrology provides a parallel warning. Sharpe et al. showed that direct specimen strain measurement is required for reliable modulus determination in thin films, while broader thin-film work by Nix emphasized the dependence of measured properties on test configuration [28,29].

Few of the supplied studies compare several periodate-treated HAMS/PVA ratios with an untreated blend at the same ratio and a neat-PVA reference under one tensile protocol. Most change several variables at once, including PVA grade, plasticizer, filler, catalyst, homogenization, or drying temperature. The present comparison of treated ratios of 1:1, 1:2, and 2:1 with untreated H1P2 and neat PVA addresses this formulation-screening gap. It does not isolate a unique molecular mechanism. The appropriate question is whether treatment and blend ratio shift the balance between nominal strength and extensibility under the present casting conditions. Any change may reflect aldehyde formation, altered hydrogen bonding, chain scission, disrupted crystallinity, retained moisture, phase continuity, or casting defects. Confirming a specific mechanism will require aldehyde quantification, spectroscopy, molecular-weight analysis, diffraction, microscopy, swelling, and wet mechanical testing. The current study therefore identifies formulation-dependent tradeoffs and priorities for confirmatory work.

3. Materials and Methods

3.1 Materials

High-amylose starch (HAMS), PVA, sodium periodate (NaIO_4), deionized water, and MD44 dialysis tubing were used. The high-amylose designation follows the laboratory record. Amylose content was not independently measured in this study. The laboratory code H identifies untreated HAMS, while S identifies sodium-periodate-treated HAMS. Supplier and lot information for HAMS and sodium periodate was not retained in the archived record.

All film preparation and tensile testing were conducted at Beijing University of Chemical Technology (BUCT), Beijing, China.

3.2 Sodium-periodate Treatment of Starch

A 4% (w/v) HAMS dispersion was prepared. For each treatment batch, 4.8 g sodium periodate was used per 4.0 g HAMS. This corresponds nominally to 0.91 mol periodate per mole of anhydroglucose unit if the stated starch mass is treated as dry starch. The mixture was held at 34 °C for 1 h under light-shielded conditions and then dialyzed in MD44 tubing for 72 h to remove low-molecular-mass reaction species and residual oxidant. The recovered material is termed sodium-periodate-treated HAMS rather than chemically verified dialdehyde starch because aldehyde content, residual periodate or iodate, and molecular-weight change were not measured.

3.3 Film Formulations and Casting

A 4% (w/v) untreated or periodate-treated HAMS stock and a 2% (w/v) PVA stock were combined to obtain the stated dry-polymer ratios shown in Table 2. The treated blends contained HAMS/PVA at 1:1 (S1P1), 1:2 (S1P2), and 2:1 (S2P1). H1P2 contained untreated HAMS/PVA at 1:2, and PVA contained no starch. Only untreated or treated HAMS, PVA, and deionized water were present in the casting mixtures. No glycerol or other plasticizer, acid catalyst, crosslinker, filler, or processing aid was added. The mixtures were solution-cast and dried at room temperature.

Independent film-sheet counts were two for S1P1, two for H1P2, four for S1P2, four for S2P1, and two for PVA. The unequal counts arose from limited material availability. Because the 4% HAMS and 2% PVA stocks were combined in different volume proportions, the total solids of the casting mixtures could vary by formulation. Wet casting volume and casting area were not retained, so dry mass per unit area could not be reconstructed. This uncertainty may have contributed to the observed thickness differences.

Table 2. Formulation identity, independent film-sheet counts, thickness records, and technical tensile-strip counts.

Code	Dry-polymer composition	Starch fraction (%)	Independent film sheets	Sheet thicknesses (mm)	Mean (mm)	Technical strip tests
S1P1	Treated HAMS:PVA, 1:1	50.0	2	0.630, 0.730	0.680	4
H1P2	Untreated HAMS:PVA, 1:2	33.3	2	0.730, 0.630	0.680	2
S1P2	Treated HAMS:PVA, 1:2	33.3	4	0.730, 0.630, 0.630, 0.600	0.6475	4
S2P1	Treated HAMS:PVA, 2:1	66.7	4	0.630, 0.660, 0.630, 0.460	0.595	4
PVA	Neat PVA	0	2	0.560, 0.630	0.595	3

Note. Thicknesses were supplied in centimeters and converted using 1 cm = 10 mm. For example, 0.063 cm = 0.63 mm. Multiple strips could originate from one sheet and are therefore not independent experimental or batch replicates.

3.4 Thickness Assignment and Tensile Testing

Tensile strips were 10 mm wide. Testing was carried out at BUCT on a Shimadzu EZ-LX universal testing machine in the 50 N configuration shown in Supplementary Figure S1. The archived reports recorded an initial grip separation of 100 mm and a crosshead speed of 10 mm min⁻¹. Maximum load and displacement at break were transcribed from each available report. The machine files contained an incorrect width entry of 1 mm. This value was replaced with the confirmed physical width of 10 mm during recalculation. Thickness values originally recorded in centimeters were converted to millimeters before computing cross-sectional area.

Where a strip-to-sheet thickness association was available (S1P2 and S2P1), the associated sheet thickness was used for that strip. For S1P1, H1P2, and PVA, the strip-to-sheet association could not be reconstructed, so the formulation mean thickness (0.680, 0.680, and 0.595 mm, respectively) was applied to every strip in that group. Laboratory-machine batch numbers 4 and 5 were reconciled with the experiment log before analysis: batch 5 was assigned to S2P1 and batch 4 to neat PVA. The report labeled 2-1 but internally labeled 1-5 was assigned to S1P1.

Nominal tensile strength, σ_{max} , was calculated from maximum load F_{max} , strip width w , and thickness t :

$$\sigma_{max} = F_{max} / (w \times t) \quad (1)$$

With load in newtons and dimensions in millimeters, the result is N mm⁻², numerically equivalent to MPa. Crosshead-derived elongation at break, $\epsilon_{b,crosshead}$, was calculated from crosshead displacement at break ΔL and the recorded initial grip separation $L_0 = 100$ mm:

$$\epsilon_{b,crosshead} = (\Delta L / L_0) \times 100\% \quad (2)$$

The term crosshead-derived is used because no extensometer or optical gauge measurement was documented. Crosshead displacement may include grip movement and test-frame compliance.

Young's modulus was not reported because the records did not establish a direct strain signal, toe-region correction, or a prespecified linear fitting interval. The procedure is therefore described as adapted from ASTM D882-21 rather than asserted to be fully compliant [27].

3.5 Data Analysis and Replication

All available technical strip tests were retained. For each formulation, results are summarized as arithmetic mean $\pm$ sample standard deviation (SD) across strip values. Because the number of independently cast sheets was small and unequal and because strip-to-sheet nesting was incomplete for three groups, no one-way ANOVA, post hoc test, confidence interval, or claim of statistical significance was applied. Percentage contrasts are descriptive and were calculated from formulation means. Individual strip values are reported in Supplementary Table S1 to keep the data structure visible.

4. Results and Discussion

4.1 Data Traceability and Specimen Dimensions

The confirmed thickness range was 0.460 to 0.730 mm, not 4.6 to 7.3 mm. The original measurements were expressed in centimeters, so 0.046 to 0.073 cm converts to 0.460 to 0.730 mm. Formulation means ranged from 0.595 to 0.680 mm (Table 2). This correction, together with the width correction from the machine-file entry of 1 mm to the confirmed 10 mm, determines the stress scale. Applying both corrections produces nominal tensile strengths of approximately 1.4 to 7.0 MPa at the strip level rather than the substantially larger values obtained from the erroneous cross-sectional dimensions.

Thickness normalization is necessary but does not remove all thickness-related effects. Drying rate, moisture gradients, voids, surface defects, and molecular orientation can vary with section thickness, and the present sheets were relatively thick compared with many commercial flexible packaging films. Consequently, the values are best interpreted as formulation-screening data for these cast specimens, not universal material constants.

4.2 Nominal Tensile Strength

Table 3. Descriptive tensile results recalculated from the corrected strip width and thickness records.

Code	Independent film sheets	Technical strip tests	Mean thickness (mm)	Nominal tensile strength (MPa)	Crosshead elongation at break (%)
S1P1	2	4	0.680	3.01 $\pm$ 0.67	31.85 $\pm$ 8.02
H1P2	2	2	0.680	5.82 $\pm$ 0.92	2.77 $\pm$ 0.21
S1P2	4	4	0.6475	1.51 $\pm$ 0.09	27.37 $\pm$ 6.71
S2P1	4	4	0.595	4.24 $\pm$ 0.73	18.12 $\pm$ 12.57
PVA	2	3	0.595	3.72 $\pm$ 0.09	128.24 $\pm$ 13.89

Note. Values are mean $\pm$ sample SD across technical strips, not independent sheet-level estimates. No inferential significance is implied.

The untreated 1:2 blend, H1P2, showed the highest descriptive mean strength at 5.82 $\pm$ 0.92 MPa. It was followed by S2P1 at 4.24 $\pm$ 0.73 MPa, neat PVA at 3.72 $\pm$ 0.09 MPa, S1P1 at 3.01 $\pm$ 0.67 MPa, and S1P2 at 1.51 $\pm$ 0.09 MPa (Table 3 and Figure 1A). H1P2 therefore cannot be described as mechanically weak based on maximum stress. Its limitation was its very low deformation before

fracture. The H1P2 SD reflects two strip values, so the group ranking should not be treated as statistically resolved.

Within the three treated formulations, mean strength increased in the order S1P2 < S1P1 < S2P1 as the treated-starch fraction rose from 33.3 to 50.0 to 66.7% of the starch-plus-PVA polymer fraction. S2P1 was 181.5% stronger than S1P2 by the ratio of group means and 14.0% stronger than neat PVA. These contrasts suggest that the treated-starch fraction influenced load bearing, but they do not isolate molecular crosslink density. Differences in casting solids, water content, thickness distribution, and defect population could contribute, particularly because the formulations were not represented by equal numbers of independent casts.

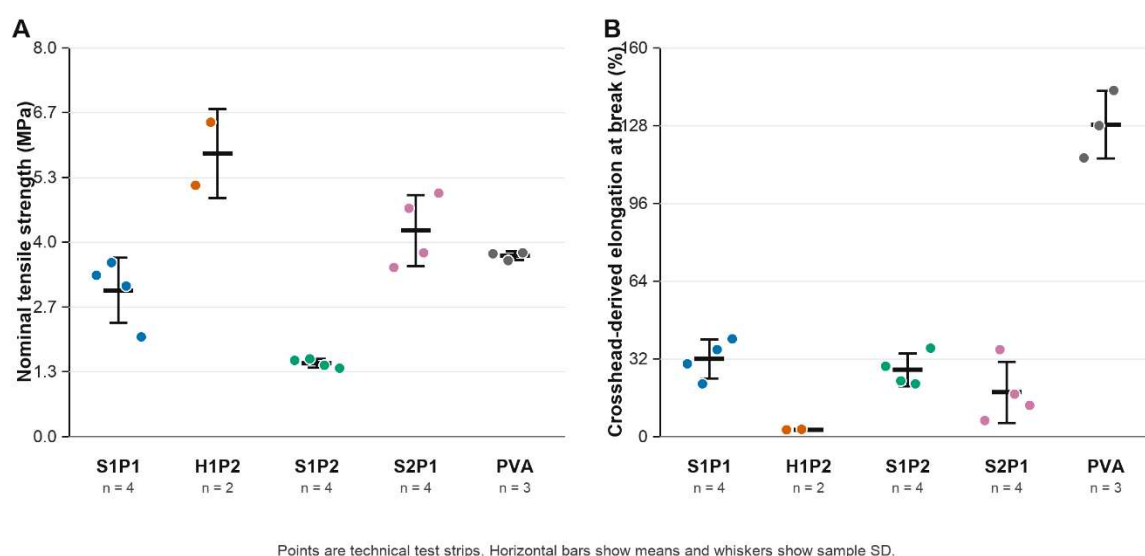


Figure 1. Recalculated (A) nominal tensile strength and (B) crosshead-derived elongation at break for sodium-periodate-treated HAMS/PVA blends, the untreated 1:2 blend, and neat PVA. Colored points show individual technical test strips. Horizontal bars and whiskers denote mean $\pm$ sample SD. Multiple strips may originate from the same independently cast sheet.

4.3 Crosshead-derived Elongation at Break

Neat PVA exhibited by far the greatest crosshead-derived elongation ($128.24 \pm 13.89\%$), whereas H1P2 failed at only $2.77 \pm 0.21\%$ (Figure 1B). The untreated 1:2 blend was therefore strong in maximum nominal stress but brittle under the present test conditions. Periodate treatment at the same 1:2 polymer ratio changed this response substantially: S1P2 reached $27.37 \pm 6.71\%$ elongation, a 9.87-fold increase relative to H1P2, while its strength fell by 74.1%. This paired comparison provides the clearest evidence that treatment shifted the mechanical balance, but it does not show that both properties improved.

Among treated blends, S1P1 had the highest mean elongation at $31.85 \pm 8.02\%$, followed by S1P2 at $27.37 \pm 6.71\%$ and S2P1 at $18.12 \pm 12.57\%$. The variation was not monotonic with composition. S2P1 was notably heterogeneous, with four strip values ranging from 6.51 to 35.72%. Such scatter may reflect sheet-to-sheet or within-sheet differences, but the incomplete nesting record prevents separation of those sources. Increasing the treated-HAMS ratio from 1:2 to 2:1 raised mean strength by 181.5% while lowering mean elongation by 33.8%. This illustrates the central tradeoff between strength and extensibility.

4.4 Descriptive Formulation Contrasts

No formulation dominated both tensile outcomes. H1P2 maximized descriptive strength but minimized elongation. PVA maximized elongation but did not maximize strength. S2P1 exceeded PVA modestly in mean strength but retained only about one-seventh of its elongation. S1P1 and S1P2

occupied intermediate positions. Selecting among these materials requires an application-specific minimum strength, allowable deformation, humidity exposure, thickness target, and failure mode. Without those design criteria, labeling any formulation as optimal would be premature.

Table 4. Prespecified descriptive contrasts derived from group means.

Contrast	Question	Strength change (%)	Elongation change (%)	Descriptive reading
S1P2 vs H1P2	Treatment at 1:2 HAMS:PVA	−74.1	+886.8 (9.87×)	Large shift toward extensibility, with lower strength
S2P1 vs S1P2	Treated-starch ratio 2:1 vs 1:2	+181.5	−33.8	Higher strength, lower elongation
S2P1 vs PVA	HAMS-rich treated blend vs neat PVA	+14.0	−85.9	Modest strength gain, major ductility loss
S1P1 vs S1P2	Treated-starch ratio 1:1 vs 1:2	+99.8	+16.3	Both means higher, without inferential testing

Note. Percentage changes use the second-listed group as the denominator. They summarize technical-strip means and are not effect estimates from an independent-cast statistical model.

4.5 Chemistry-aware Interpretation

The established first step of periodate chemistry is oxidative cleavage of the bond between C2 and C3 at a vicinal diol site in an anhydroglucose unit. This is not cleavage of an α -1,2-glycosidic linkage. The reaction produces ring-opened aldehyde-type sites. In aqueous polysaccharides, the resulting carbonyls can be hydrated and can form hemiacetal structures. Reactions with PVA hydroxyl groups are chemically possible under suitable conditions, and an acid-catalyzed heated study provides direct precedent [15].

The present data do not confirm that a covalent pathway governed tensile behavior. No iodometric aldehyde assay, carbonyl analysis, FTIR, NMR, gel fraction, swelling experiment, molecular-weight measurement, X-ray diffraction, thermal analysis, or microscopy was performed. No acid catalyst or other crosslinking reagent was used, and the films were dried at room temperature. Hydrated carbonyl and hemiacetal equilibria remain chemically plausible, but extensive stable acetal crosslinking between treated HAMS and PVA cannot be assumed. Statements that the treatment formed acetal bonds or improved interfacial compatibility would exceed the evidence.

The decrease in strength and increase in elongation for S1P2 relative to H1P2 are compatible with greater chain mobility or fewer effective load-bearing domains. Periodate-induced ring opening and chain scission could disrupt starch ordering or reduce molecular weight. Changes in bound water or residual low-molecular-mass species could further plasticize the blend. The recovery of strength at the 2:1 ratio could arise from a larger fraction of HAMS-rich load-bearing material, altered phase continuity, or more intermolecular contacts. Hydrogen bonding and possible aldehyde-hydroxyl reactions may contribute, but the nonmonotonic elongation and absence of chemical characterization prevent a unique assignment.

Earlier starch/PVA studies also show that compatibility cannot be inferred from tensile strength alone. Spectroscopy and microscopy have linked composition to hydrogen bonding, crystallinity, and phase organization [8-13]. Alternative oxidation and nanoparticle systems demonstrate that added functionality can strengthen one property while weakening another [14,17-20]. The current results fit that broader pattern of coupled tradeoffs rather than demonstrating a single crosslink-controlled mechanism.

Because no external plasticizer was added, retained water may have contributed to chain mobility and to the high elongation of neat PVA. Moisture content was not measured. This uncertainty is important because both HAMS and PVA are hydrophilic and their tensile responses can change substantially with humidity.

4.6 Relevance to Packaging and Study Limitations

The tensile results provide a useful first screen for film development, but they are insufficient to claim suitability for lightweight food packaging. Packaging performance also depends on water-vapor and oxygen transmission, liquid-water resistance, optical clarity, sealability, puncture and tear resistance, creep, dimensional stability, migration, odor, thermal behavior, storage aging, and performance across humidity and temperature [1-3,6,8,9,13,15,17,18]. The current sheets were 0.46 to 0.73 mm thick. Translating the formulation to a thinner, continuously produced film could change drying morphology and mechanical response.

Biodegradability and environmental benefit were not tested. PVA degradation is strongly environment-dependent, and disappearance or seawater disintegration is not equivalent to mineralization [21,23-25]. The renewable starch fraction is relevant to formulation design, but it does not establish lower life-cycle impact, compostability, marine biodegradability, recyclability, food-contact compliance, or freedom from ecotoxic residuals. Those claims require standardized tests. Food-contact use also requires migration and regulatory evaluation.

The mechanical design also limits inference. Independent cast counts were small and unequal. Technical strips were used as the descriptive unit, and strip nesting was incomplete for S1P1, H1P2, and PVA. Formulation-mean thickness was substituted for those strips. Conditioning and moisture content were not documented, while the absence of added plasticizer was confirmed. Strain came from crosshead travel. These limitations preclude formal significance testing and reliable Young's modulus estimation. A confirmatory study should use at least three independently prepared batches per formulation, sample multiple strips per batch, preserve strip-to-batch and pointwise-thickness identifiers, condition films under controlled humidity, and analyze the nested data with batch as the experimental unit.

5. Conclusion

Correcting the specimen geometry to a 10 mm width and converting the recorded thicknesses from centimeters to millimeters yielded a defensible nominal stress scale for the five film formulations. The untreated 1:2 HAMS/PVA blend had the highest descriptive strength at 5.82 ± 0.92 MPa but the lowest elongation at $2.77 \pm 0.21\%$. Periodate treatment at the same ratio reduced strength to 1.51 ± 0.09 MPa and increased crosshead-derived elongation to $27.37 \pm 6.71\%$. This was a shift toward extensibility rather than a simultaneous improvement in both outcomes. Increasing treated HAMS to a 2:1 ratio restored strength to 4.24 ± 0.73 MPa, which was 14.0% above neat PVA. Its elongation remained 85.9% lower than that of PVA.

These results establish a formulation-dependent tradeoff between strength and extensibility and do not identify a universal optimum. Periodate chemistry offers plausible routes through aldehyde formation, altered chain packing, hydrogen bonding, and possible aldehyde-hydroxyl reactions, but covalent acetal or hemiacetal bonding was not demonstrated. The next decisive experiments are chemical verification of oxidation, independent-batch replication, humidity-conditioned tensile testing with direct strain measurement, and barrier, water-resistance, migration, thermal, and biodegradation assessments. Until those data are available, the formulations should be described as candidates for further packaging-film development rather than validated replacements for commercial packaging plastics.

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Competing interests

None

Data availability

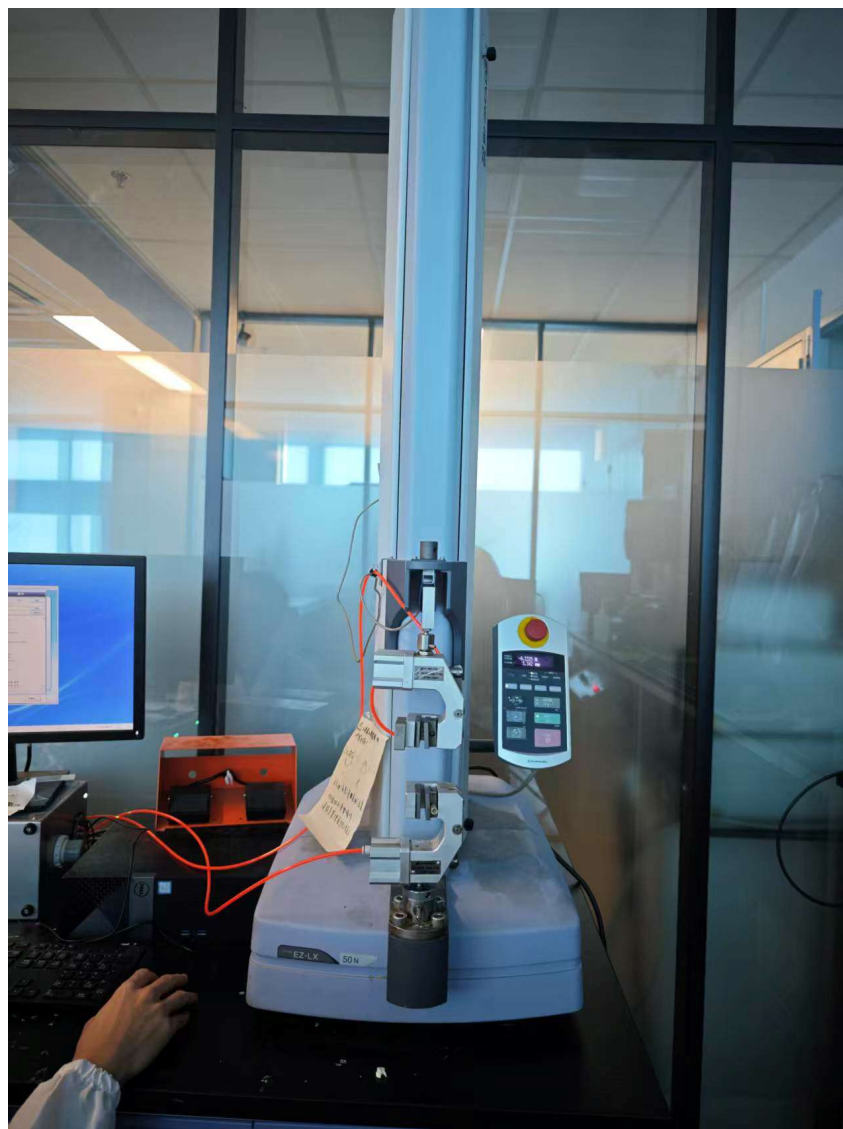
Raw tensile machine reports, transcribed strip-level data, calculation rules, and the manuscript dataset are available from the corresponding author, subject to repository deposition and completion of identifying metadata.

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Supplementary information



Supplementary Figure S1. Shimadzu EZ-LX tensile testing system in the 50 N configuration used at Beijing University of Chemical Technology.

Supplementary Table S1. Strip-level tensile data

Supplementary Table S1 reports the machine maximum load and displacement at break together with the thickness used for each calculation. These values make the geometry correction and technical-replication structure auditable. Labels are normalized to the reconciled laboratory batch numbers.

Supplementary Table S1. Individual technical-strip results used in the descriptive analysis.

Formulation	Strip	Fmax (N)	Break displacement (mm)	Thickness used (mm)	Strength (MPa)	Elongation (%)
S1P1	1-1	22.5683	29.8175	0.680	3.319	29.817
S1P1	1-2	24.3289	21.6231	0.680	3.578	21.623
S1P1	1-3	21.0230	35.8091	0.680	3.092	35.809
S1P1	1-5	13.9029	40.1356	0.680	2.045	40.136
H1P2	2-2	35.1562	2.6220	0.680	5.170	2.622
H1P2	2-3	43.9582	2.9259	0.680	6.464	2.926
S1P2	3-1	11.4185	28.8331	0.730	1.564	28.833
S1P2	3-2	10.0672	22.7538	0.630	1.598	22.754
S1P2	3-3	9.2017	21.6496	0.630	1.461	21.650
S1P2	3-4	8.4060	36.2563	0.600	1.401	36.256
S2P1	5-1	21.9085	6.5129	0.630	3.478	6.513
S2P1	5-2	30.9836	35.7249	0.660	4.694	35.725
S2P1	5-3	23.7867	17.4486	0.630	3.776	17.449
S2P1	5-5	23.0454	12.7771	0.460	5.010	12.777
PVA	4-1	22.3915	114.5310	0.595	3.763	114.531
PVA	4-2	21.5051	127.9020	0.595	3.614	127.902
PVA	4-3	22.4707	142.3000	0.595	3.777	142.300

Note. S1P1, H1P2, and PVA use formulation-mean thickness because strip-to-sheet thickness assignment was unavailable. S1P2 and S2P1 use the associated sheet thickness. Fmax, maximum load.