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In situ crosslinked Schiff base biohydrogels containing *Carica papaya* peel extract: application in the packaging of fresh berries†

Ganeswar Dalei,[a] Swagat Kumar Das,[b] Susri Sangita Mohapatra[c] and Subhraseema Das *[ac]

Although endowed with antimicrobial and antioxidant properties, fruit peel is often regarded as waste. With the focus largely on sustainable development and sustainability, this study explores the valorisation of aforesaid waste. In this work, the influence of *C. papaya* peel powders on the functional properties of Schiff base hydrogels of chitosan (Cs) and dialdehyde starch (DAS) was investigated for active food packaging. In this work, the hydrogels were fabricated by virtue of *in situ* crosslinking of −CHO moieties of DAS and $-NH_2$ groups of Cs. The utilization of *C. papaya* peel extract in hydrogel films enhanced their thickness, moisture content and opacity. Furthermore, the developed hydrogel film offered versatile performances in terms of antimicrobial and antioxidant activities, water-barrier properties, high tensile strength, stretched/twisted flexibility, anti-puncture resistance, thermal stability and biodegradability. Noteworthy, the shelf life of fresh blueberries, strawberries, gooseberries and Indian jujube was extended by at least one week upon packaging with the fabricated material as compared with unpackaged ones. Thus, our work paves the path for the design of a versatile hydrogel film for potential food packaging and preservation.

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Sustainability spotlight

The present study highlights the valorization of *Carica papaya* peel extract towards the fabrication of biohydrogels for the packaging of fresh berries. *In situ* formed Schiff base hydrogels composed of dialdehyde starch and chitosan were fabricated and the peel extract was incorporated into the matrix. The utilization of the *C. papaya* peel extract in the film enhanced its thickness, moisture content and opacity. Furthermore, the developed hydrogel offered versatile performances in terms of antimicrobial and antioxidant activities, water-barrier properties, high tensile strength, stretched/twisted flexibility, anti-puncture resistance, thermal stability and biodegradability. The shelf life of fresh blueberries, strawberries, gooseberries and Indian jujube were extended by at least one week upon packaging with the fabricated biohydrogels as compared with the unpackaged ones. Thus, the developed biohydrogel films ensure enhanced shelf lives of the berries and show potential as sustainable packaging materials.

1. Introduction

With the world population striking 8 billion on 15 November 2022 and projected to escalate to 8.5 billion by 2030,[1] the need for food supply shall inevitably surge. To keep up with the rising food demand, the generation of food packaging materials will predictably rise. Indisputably, plastics are still the most desirable choice for packaging materials as they are cheaper and can be attuned to different packaging formats. However, the overwhelming use of plastic packaging in food industries has not only led to alarming environmental concerns, but also startled the scientific community from the data pertaining to human consumption of microplastics.[2] Thus, the food industry is in urgent need of promising materials that will altogether be a superior alternative to plastics. Besides their biodegradable and sustainable nature, such materials should be endowed with functionalities in terms of antioxidants or antimicrobials to prevent food spoilage and enhance their quality and shelf life.

Polymeric hydrogels have been on the fore towards the fabrication of food packaging materials, as they are bestowed with a suitable conformation that regulates the moisture generated by food products.[3] Hydrogel applications in the food sector have seen an upward trend as hydrogel is a viable alternative to plastics for preventing food spoilage. Their inherent attributes such as swelling, mechanical integrity and biodegradability render them as commendable choices compared to

[a]Department of Chemistry, Odisha University of Technology and Research, Bhubaneswar 751029, Odisha, India. E-mail: subhraseema@ravenshawuniversity.ac.in; subhraseema@gmail.com

[b]Department of Biotechnology, Odisha University of Technology and Research, Bhubaneswar 751029, Odisha, India

[c]Department of Chemistry, Ravenshaw University, Cuttack 753003, Odisha, India

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conventional packaging. With judicious choice of parent polymers, the designed hydrogels have been bestowed with improved gas/vapour barrier properties and antimicrobial activities.[4] Of particular interest are the bio-inspired polysaccharide hydrogels that find prominence today owing to their noble attributes such as nontoxicity and biodegradability.[4] Literature is invariably abound with reports signifying the high relevance of natural polysaccharides such as chitosan,[5] cellulose,[6] pectin,[7] alginate,[8] guar gum,[9] xanthan gum,[10] gellan gum,[11] and gelatin[12] in active food packaging.

Nonetheless, one of the major shortcomings associated with hydrogels is their low stability when subjected to some stimuli.[4] In order to overcome this limitation, the incorporation of compounds, mainly natural extracts from peels of fruits and vegetables, has allured researchers. Such compounds are associated with an array of bioactive functionalities such as polyphenols, sugars, terpenes, and carotenoids that play a vital role in engineering the hydrogels for various applications. The phenolic compounds, in particular, have attracted significant attention as they show great potential as antioxidant, anticancer, antibacterial, and anti-biofilm agents in the fields of health and environment.[13,14] Diverse studies have reported active food packaging hydrogels designed from the extracts of pomegranate peels,[15] green tea,[16] neem,[17] shallot wastes,[18] banana leaves,[19] black grapes,[20] and potato peels.[21]

Papaya (*Carica papaya* L.) belonging to the Caricaceae family is a popular fruit with great health benefits and cultivated mostly in tropical regions. Papaya is enriched with a plethora of bioactive compounds that are highly important in human diet. Thus, it comes as no surprise that papaya harvesting generates tremendous wastes, mostly in the form of peels. Conventionally, these papaya peels (PPs) have been used in cattle feed, nutraceutical supplements and domestic remedies. However, with the booming knowledge on the importance of natural extracts, the utilization of PPs to develop value-added products has provoked researchers. Endeavours in this direction has led to the valorization of PPs as biofuels, dietary fibers and biomaterials.[22] PP extract (PPE) has also been effectually utilized as a corrosion inhibitor for aluminium alloy.[23] A couple of reports have noted the efficacy of gelatin and PPE hydrogels in packaging.[24,25]

Starch and chitosan are two important biopolymers that are widely used in the food processing sector.[26] Although the aforesaid polymers have several advantages in food packaging,[26] when used alone they suffer from poor mechanical properties. Hence, we combined these two biopolymers to alleviate the disadvantages in the use of hydrogels derived from monolithic materials. Currently adopted hydrogel synthesis strategies have often relied on the use of chemical crosslinking reagents to accomplish a three-dimensional network structure. With the focus on green chemistry looming large today, a bio-based crosslinker will be beneficial in the long run. Of late, hydrogels employing *in situ* crosslinking Schiff base bonds have garnered prominence owing to their high sensitivity, good recyclability and fast response to external stimuli.[27] To be specific, the oxidation of natural polysaccharides by periodates has gained substantial interest. First, the synthesis ensues a bio-based material, and second, the periodate can be recycled.[28] In addition, these aldehyde groups serve as crosslinking hotspots for a variety of other chemical reactions. One such promising reaction that has gained eminence is the Schiff base forming crosslinking reaction utilizing imine bonds. Thus, in this context, we prepared *in situ* crosslinked Schiff base hydrogels devoid of any external crosslinkers.

In the present research contribution, *in situ* forming Schiff base hydrogels of starch and chitosan were explored for their utility as potential food packaging materials. First, pristine starch was functionalized to dialdehyde starch (DAS) *via* periodate oxidation. The Schiff base hydrogel resulted from the crosslinking of aldehyde groups of DAS and amino groups of chitosan (designated as CsDAS hydrogel). An active food packaging system was developed by incorporating the *C. papaya* peel extract into the hydrogels. The hydrogel characteristic parameters and its utility in extending the shelf life of berries were evaluated (Scheme 1).

2. Materials and methods

2.1. Materials

Cs (de-acetylation degree > 75%) and starch were obtained from Sigma Aldrich, India and used as received. We estimated M_v, which is the viscosity-average molecular mass of Cs, to be 1.78×10^5. The detailed procedure for the estimation of M_v is reported in our earlier published paper.[29] All other reagents procured from Sigma-Aldrich (India) and/or HiMedia Laboratories (India) were of the highest purity and used without further purification.

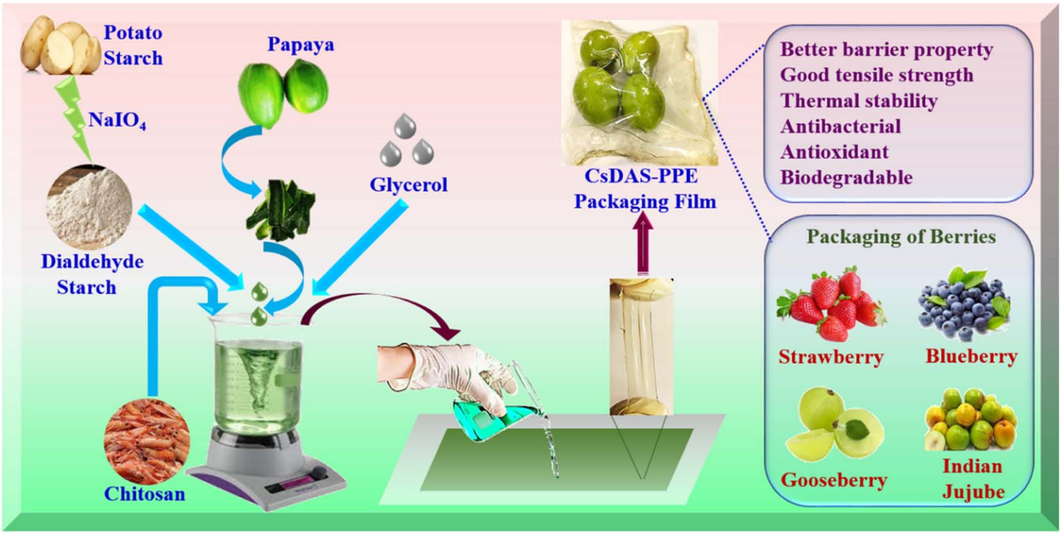
2.2. Preparation of PPE and analysis by GCMS

Green papayas were purchased from the local market in Cuttack, Odisha and peeled. The papaya peel extract (PPE) was obtained by a method reported in the literature;[15] the detailed procedure is presented in Section S2 in ESI.† The phytochemical analysis of PPE was performed using a GC-MS system (Agilent 7890B GC coupled with 5977A MSD). The experimental conditions were set as: 1 μL injection volume; splitless injection; oven programmed for 50 °C (1 min hold) at a rate of 5 °C per min to 300 °C (5 min hold). He carrier gas was set as: flow rate: 1 mL min^{-1}; purge flow: 3 mL min^{-1}. Data analysis was performed by MSD Chem Station Data and compared with the standard NIST14 Library.

2.3. Preparation of DAS, CsDAS, and CsDAS-PPE hydrogels

Dialdehyde starch (DAS) was obtained by the conventional periodate oxidation method.[30] The yield and aldehyde content were determined by a method reported previously.[31]

For hydrogel preparation, 2 wt% Cs solution was prepared in 0.1 M acetic acid. Then, the DAS solution (1 wt%) was dissolved separately in water. Both the polymer solutions were mechanically agitated at 350 rpm for 3 h to allow for *in situ* crosslinking. The obtained mixture solution was casted and dried *in vacuo*. For PPE-incorporated hydrogels, the PPE was added at three different concentrations of 1%, 3%, and 5% (w/v) into the



Scheme 1 Diagrammatic depiction of the fabrication of chitosan (Cs)-dialdehyde starch (DAS) Schiff base hydrogels containing *C. papaya* peel extract (CsDAS-PPE hydrogel) as novel packaging materials for fresh berries.

CsDAS solution and stirred for 30 min to ensure proper homogenization. The samples, designated as CsDAS1, CsDAS3, CsDAS5 respectively, were dried in a similar manner as described earlier. In all the prepared samples, glycerol (1% w/v) was added as a plasticizer.

2.4. Characterization

The thickness, moisture content, solubility and opacity of the CsDAS and CsDAS-PPE hydrogels were estimated as per the procedures reported in the literature.[25] The water vapour permeability (WVP) and oxygen permeability (OP) were determined by a method reported in the literature.[32] The FTIR spectra were recorded using a Thermo Nicolet iS5 FTIR spectrophotometer. The morphology was examined using a field emission scanning electron microscope (Carl Zeiss-Gemini FESEM 300). Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 at a temperature ranging from ambient to 1000 °C in a N_2 atmosphere. For the mechanical tests, the hydrogel films of dimensions (50 mm × 15 mm) were equipped with a 1 kN load cell and a strain rate of 10 mm min^{-1} was employed in an Instron 5567 (Instron, USA) at room temperature of 25 °C. The methodologies are presented in Sections S3–S5 in ESI.†

2.5. Antimicrobial studies

In this study, the disc diffusion method was employed.[25] The antimicrobial effects of the hydrogels against *Escherichia coli* and *Micrococcus lysodeikticus* were estimated by taking 5 mm discs of the hydrogels and investigating the zones of inhibition against the respective pathogens. All experiments were performed in triplicate.

2.6. Antioxidant studies

The antioxidant properties of the hydrogels were examined for their TPC and DPPH radical scavenging activities as reported in the literature.[25] The data are presented as mean ± SD of three independent readings.

2.7. Biodegradation test

The extent of biodegradability of the prepared hydrogels was studied by the soil burial method as reported in the literature.[18] The hydrogels (approximately weighing 0.5 g) were buried in 100 g soil and the change in weight was measured at specific intervals. The detailed method is presented in Section S6 in ESI.†

2.8. Application in preservation of fresh berries

The potential of the prepared hydrogels as packaging materials was investigated by wrapping them on strawberries, gooseberries, Indian jujube and blueberries procured locally. Prior to the conduction of experiment, the berries were thoroughly washed to get rid of any traces of dirt or impurity. Packages were made (15 cm × 15 cm) by heat sealing. For every package, four small holes were punctured to enable cell respiration. Subsequently, berries were segregated into four batches according to their type; control batch without any packaging, berries were wrapped with a commercially available polyethylene film, a CsDAS film and a CsDAS5 film. For each berry type, five replicate packages were prepared and noted for their freshness during the experimental tenure. Ambient storage conditions were maintained throughout (25–28 °C). Berries with any signs of contamination or brown spots were considered for the calculation of fungal decay. According to Zhao *et al.*[33] the rate of fungal decay (%) was calculated as: (the number of decayed fruits/total number of fruits) × 100. The weight loss (%) was measured as: (initial weight − final weight)/initial weight × 100, where the initial weight refers to the original weight of the berries and the final weight is the weight of the respective berries after storage.[33] For strawberries in particular, the titratable acid content and total soluble solid content were also evaluated by previously reported methods.[33,34] The evaluation parameters were monitored every day for each group and determined in triplicate.

3. Results and discussion

3.1. GC-MS analysis of *C. papaya* peel extract

The compositional analysis was performed by GC-MS and the phyto-compounds were identified from the matches in the mass spectra in the NIST14 library. The phytochemicals present in the *C. papaya* peel extract with their corresponding retention time (RT), molecular formula (MF) and molecular weight (MW) are presented in Table 1. The GCMS profiling revealed the presence of an array of metabolites, as projected in Table 1, that include fatty acids, esters, alkanes, alkenes, tocopherols and sterols. Previous reports on the *C. papaya* leaf, fruit, seed and peel extracts have also demonstrated the presence of a wide variety of bioactive compounds that have exhibited antimicrobial, antioxidant, anticancer and other medicinal properties.[35–38]

3.2. Synthesis and FTIR spectral analysis of DAS

Periodate oxidation selectively cleaves the carbon–carbon bond of vicinal –OH groups of the glucopyranose residues, resulting in the ring opening of the polysaccharide. In our study, starch was selectively oxidized to form dialdehyde starch (DAS) (Fig. 1A). The yield and degree of oxidation were evaluated to be 88.66% and 42% respectively. Fig. 1B illustrates the FTIR spectra of starch and DAS. Pristine starch showed a broad band around 3500–3000 cm^{-1} attributed to the hydroxyl stretching vibration and a band at 1640 cm^{-1} assigned to the scissoring of two O–H bonds of absorbed water molecules.[39] However, besides the aforementioned peaks, there appeared a new peak at 1735 cm^{-1} in the spectrum of DAS, which is the characteristic absorption peak of C=O vibrations of aldehyde groups in DAS.[40] In addition, a sharp band is clearly evident around 750 cm^{-1} in the spectrum of DAS. This could be ascribed to the C–H out-of-plane bending arising from the formation of hemiacetals between –CHO and –OH groups.[41] Thus, the FTIR analyses validated the formation of DAS.

3.3. Schiff base hydrogel formation

Fig. 2A depicts the plausible scheme of Schiff base hydrogel formation between Cs and DAS. The CsDAS hydrogel was accomplished *via* the *in situ* Schiff base reaction, which was ascertained from the peak at 1635 cm^{-1} in the FTIR spectrum of CsDAS (Fig. 2B). This peak is attributed to the C=N linkages (imine bonds) of the Schiff base reaction between the aldehyde and amine. After the addition of *C. papaya* peel extract (PPE) into the CsDAS films, no new peaks or significant wavelength shifts were observed, indicating the absence of any covalent bonds between PPE and CsDAS.[42] Thus, it could be inferred that the interaction between CsDAS and PPE was likely a physical response. It was also witnessed that the broad peak around 3400 cm^{-1} flattened with the increase in PPE content, which indicated the increasing hydrogen bonds between the

Table 1 Phytochemicals identified in the *C. papaya* peel extract by GC-MS

Sl. No.	RT (min)	Phytocomponents[a]	MF	MW
1	3.221	17-Octadecynoic acid	$C_{18}H_{32}O_2$	280
2	3.749	Octadecanoic acid	$C_{18}H_{36}O_2$	284
3	4.398	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256
4	5.505	Tetradecanoic acid	$C_{14}H_{28}O_2$	228
5	5.734	Oleic acid	$C_{18}H_{34}O_2$	282
6	10.824	9-Decenoic acid	$C_{10}H_{18}O_2$	170
7	14.507	Phytol	$C_{20}H_{40}O$	296
8	15.149	p-Xylene	C_8H_{10}	106
9	16.136	Phytol acetate	$C_{22}H_{42}O_2$	338
10	19.005	Campesterol	$C_{28}H_{48}O$	400
11	19.826	Limonene 1,2-epoxide	$C_{10}H_{16}O$	152
12	20.672	Squalene	$C_{30}H_{50}$	410
13	21.225	Stigmasterol	$C_{29}H_{48}O$	412
14	21.357	Tetracosanoic acid	$C_{24}H_{48}O_2$	368
15	22.072	Tetracosanoic acid, methyl ester	$C_{25}H_{50}O_2$	382
16	23.231	Tetradecyl alcohol	$C_{14}H_{30}O$	214
17	23.79	γ-Sitosterol	$C_{29}H_{50}O$	414
18	24.520	Linoleic acid, phenylmethyl ester	$C_{25}H_{38}O$	370
19	25.667	Hexadecanoic acid, isopropyl ester	$C_{19}H_{38}O_2$	298
20	30.114	1-Hexacosene	$C_{26}H_{52}$	364
21	30.776	1-Tetradecyl acetate	$C_{16}H_{32}O_2$	256
22	31.232	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$	284
23	31.711	Oleic acid	$C_{18}H_{34}O_2$	282
24	32.069	10-Undecenal	$C_{11}H_{20}O$	168
25	33.332	Hexadecanoic acid, 2,3-dihydroxypropyl ester	$C_{19}H_{38}O_4$	330

[a] Compounds identified at 90% similarity with the standard mass spectra in NIST 14 library. RT: retention time; MW: molecular weight; MF: molecular formula.

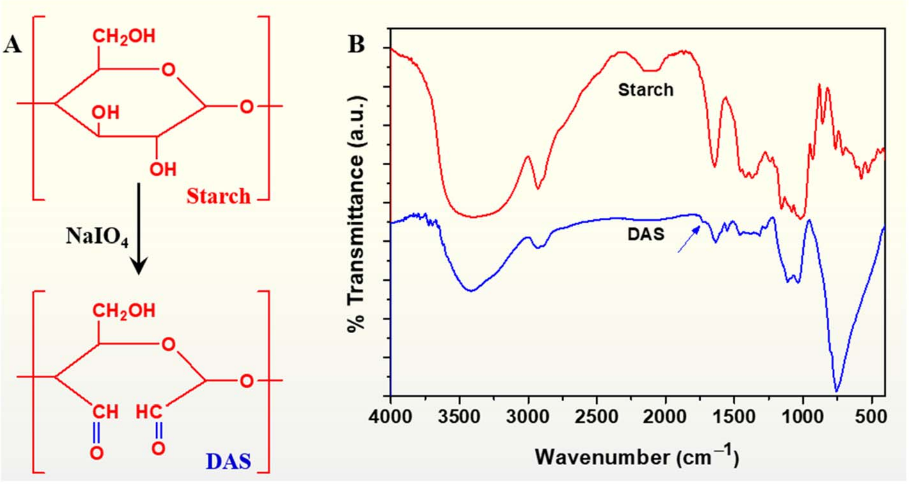


Fig. 1 Oxidation of starch to dialdehyde starch (DAS). (A) Representation and (B) FTIR spectra of starch and DAS.

polyphenols of PPE and the –OH or –NH groups of the CsDAS hydrogel.[43,44] Therefore, the FTIR spectral data affirmed the formation of CsDAS hydrogel and signified the interaction of the *C. papaya* peel extract with the parent hydrogel.

3.4. Physical properties of hydrogel packaging films

Various physical properties of the constructed CsDAS and CsDAS-PPE hydrogel films in terms of their appearances, thickness, moisture content, solubility, swelling, permeability to water and oxygen and their opacity were estimated, and the results are presented in Table 2.

3.4.1. Film appearance and thickness. In the visual depiction (Fig. 3A), the blank CsDAS hydrogel was transparent and devoid of any color. However, with the increase in PPE content in the hydrogels, a greenish tinge develops gradually, which is the color of the extract originally. We could further witness that the thickness of the hydrogel films gradually increased with the increase in PPE concentration. The thickness varied from 0.083 mm to 0.117 mm with a significant difference ($p \leq 0.05$) (Table 2). This observation might be attributed to the incomplete dissolution of the PPE powder in the hydrogel emulsion, as it is composed of both soluble and insoluble fibers.[45] This result was further justified from the SEM images (Fig. 3B), which revealed the presence of solid particles embedded on the hydrogel surface incorporated with PPE. Literature reports also point to similar changes in thickness with the addition of such extracts.[25,46]

3.4.2. Physical characteristics of hydrogel films. From Table 2, an enhancement in the moisture content and water solubility of the PPE-incorporated hydrogel films is evident in comparison to the blank hydrogel film. The *C. papaya* peel

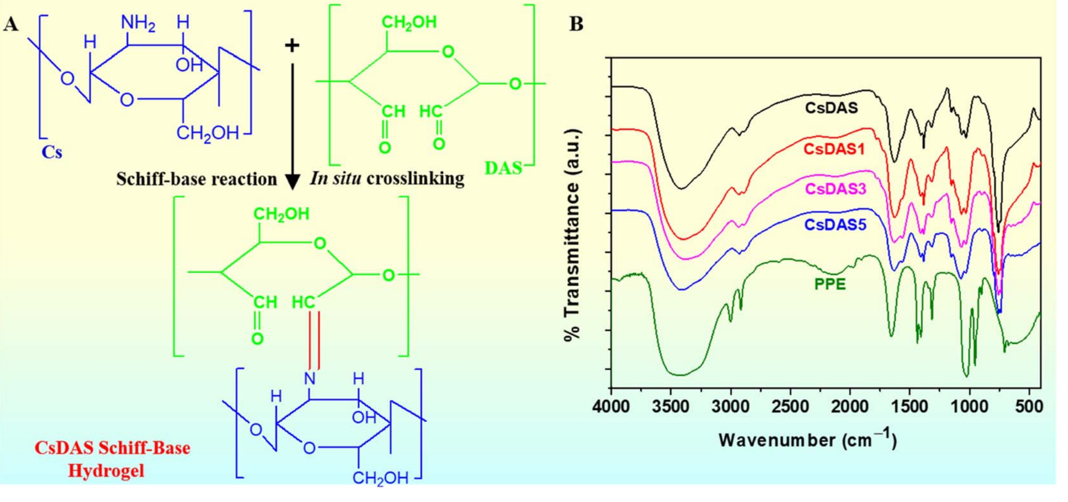


Fig. 2 (A) Schematic of the Schiff base CsDAS hydrogel formation from chitosan (Cs) and dialdehyde starch (DAS) and (B) FTIR spectra of the *C. papaya* peel extract (PPE), CsDAS hydrogel and *C. papaya* peel extract-incorporated hydrogel films at 1% (CsDAS1), 3% (CsDAS3), and 5% (CsDAS5).

Table 2 Summary of the physical parameters of the packaging films[a]

Films	Thickness (mm)	Moisture content (%)	Water solubility (%)	Swelling (%)	WVP × 10^{-11} (g ms^{-1} Pa^{-1})	OP × 10^{-6} (g per day m^{-1} Pa^{-1})	Opacity
CsDAS	0.083 ± 0.01^{a}	17.31 ± 0.05^{b}	57.33 ± 0.04^{a}	177.33 ± 11.14^{c}	8.6 ± 0.05^{b}	7.2 ± 0.11^{a}	0.66 ± 0.15^{c}
CsDAS1	0.097 ± 0.01^{d}	20.21 ± 0.11^{a}	60.27 ± 0.81^{c}	280.66 ± 20.31^{d}	8.1 ± 0.09^{c}	6.7 ± 0.13^{c}	1.06 ± 0.11^{b}
CsDAS3	0.109 ± 0.01^{b}	22.13 ± 0.07^{c}	62.44 ± 0.13^{d}	355.21 ± 19.23^{a}	7.5 ± 0.11^{a}	6.1 ± 0.21^{b}	1.17 ± 0.13^{a}
CsDAS5	0.117 ± 0.01^{c}	25.22 ± 0.11^{d}	68.33 ± 0.11^{b}	419.07 ± 23.51^{b}	7.2 ± 0.05^{d}	6.0 ± 0.05^{d}	1.26 ± 0.11^{d}

[a] Data presented as mean ± SD ($n = 3$) and the superscripts in the same column indicate significant differences ($p \leq 0.05$) between the samples. CsDAS is the blank hydrogel film; CsDAS1, CsDAS3, CsDAS5 are the hydrogel films incorporated with *C. papaya* peel extract at 1%, 3%, 5% respectively. WVP is water vapour permeability and OP represents oxygen permeability.

extract comprises various hydrophilic and hydrophobic polyphenols (as presented in Table 1), which, when added to the hydrogel emulsions, largely influences the aforementioned parameters. The pristine CsDAS hydrogel film exhibited a moisture content close to 17.31%. However, the moisture content increased with higher PPE concentrations. The water solubility also displayed the same trend. This could be explained by the improved hydrophilic nature of CsDAS films, which also marks its higher swelling, as shown in Table 2. The incorporation of PPE into the hydrogel matrix facilitated the water content of the films possibly due to the interactions between the polysaccharides and polyphenols of the extract.[47] As per a report by Sun and team, such an enhancement in the swellability of the films added with fruit peel extracts may be ascribed to the enhanced networking between the hydrophilic groups of the extracts with water molecules.[43]

3.4.3. Permeability of hydrogel films. One of the crucial aspects of a food packaging film is preventing/retarding food deterioration. Water vapour permeability (WVP) and oxygen permeability (OP) are important parameters to assess the aforementioned permeation at a given temperature. To maintain the freshness of foods, the WVP should be retained as low as feasible. The data marked that inclusion of PPE had a diminutive influence on the WVP and OP of the CsDAS films. This reduction with the increase in PPE content suggested that the addition of PPE enhanced the water and oxygen barrier properties of the films, which may likely be ascribed to the increased film thickness (Table 2). As a result, the water vapour and/or oxygen molecules are blocked easily, *i.e.* the permeation time is longer. It is well established that the polyphenols in the PPE may induce interaction with the films, which resulted in restricting the interactions between hydrophilic groups of CsDAS and water oxygen molecules, thereby improving the barrier properties.[48,49]

3.4.4. Opacity of hydrogel films. The color and opacity remain explicit factors that directly impact the consumer acceptance rate for the developed packaging films. The opacity of the hydrogel films is listed in Table 2. The neat CsDAS hydrogel film had higher transparency (seen from Fig. 3A) and opacity than those of the others. After the addition of PPE, the opacity was significantly ($p < 0.05$) increased. As a result, the packaged foods ensured protection from the visible and UV radiation that lead to losses in flavour and nutrition index.[49] Thus, the results indicate that the CsDAS5 hydrogel is endowed

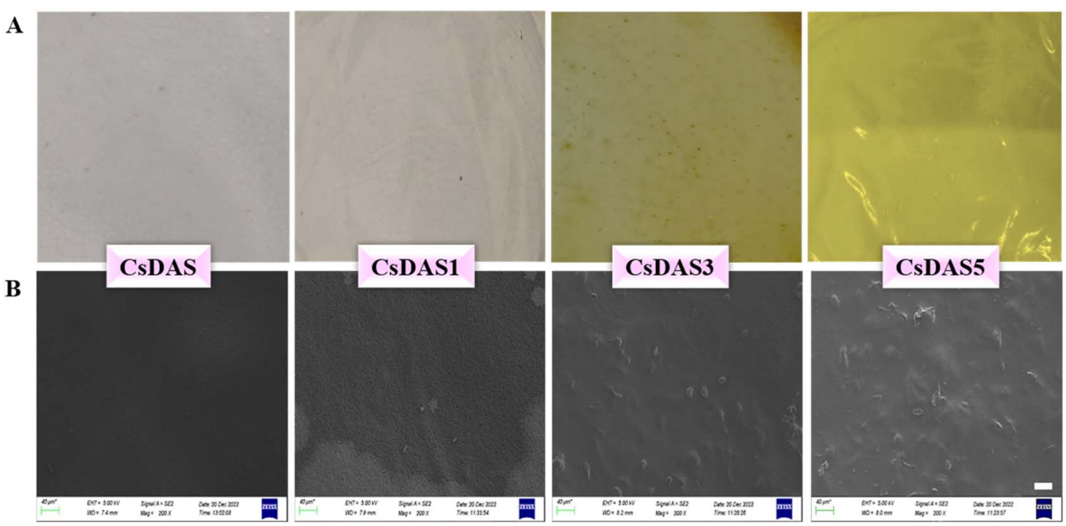


Fig. 3 (A) Photographs and (B) FESEM images (scale bar = 40 μm) of the chitosan-dialdehyde starch (CsDAS) film and *C. papaya* peel extract-incorporated films at 1% (CsDAS1), 3% (CsDAS3), and 5% (CsDAS5).

with higher opacity and better color (from Fig. 3A) that validate its potential as a wrapping food material.

3.5. Mechanical analysis of hydrogel packaging films

In practical scenarios, the lifespan of food packaging films is recommended by their mechanical properties. Visually, the stretched CsDAS5 hydrogel film quite clearly depicted impressive stretching and twisting deformations, as shown in Fig. 4A and B respectively. The anti-puncture characteristic offered by the CsDAS5 hydrogel packaging film is also evident from Fig. 4C. The mechanical parameters in terms of E modulus, tensile strength and elongation at break (ε%) are presented in Table 3. The optimal elastic properties are displayed by the CsDAS5 hydrogel packaging film. ε% is the decisive factor for a material to acquire flexibility or brittleness. The CsDAS5 hydrogel film has better ε% and tensile strength properties among the lot. This observation could be probably attributed to the greater interaction of polyphenols in PPE with biopolymers, which may alter the hydrogen bond formation and impart stiffness to the film.[18] Earlier studies reported similar effects for hydrogel films with apple peel and ginseng extracts.[50,51] Thus, taken altogether, the aforementioned virtues including the mechanical strength, ε%, deformation and anti-puncture resistance put forth the high significant application of the CsDAS5 hydrogel in packaging films.

3.6. Thermal analysis of hydrogel packaging films

The thermogravimetric curves of chitosan, starch and DAS are displayed in Fig. 5A. Both Cs and starch began to decompose at about 300 °C, as witnessed in Fig. 5A. For DAS, the thermal decomposition occurred at about 190 °C and was quite slow with almost 40% remaining. This lowering in the decomposition temperature of DAS might be justified by the pyranose ring-opening in DAS upon oxidation leading to the destruction of the original structure of starch [52]. Such thermal behaviour for DAS has been reported previously.[40,52–54] From the TG curves in Fig. 5B, it could be seen that the decomposition temperature for the hydrogels loaded with the *C. papaya* peel extract is higher than that of the neat CsDAS hydrogel. The CsDAS5 hydrogel film revealed a higher thermal stability among all the other specimens that might be associated with the hydrogen bonding interactions of the polyphenols of PPE with the biopolymer.

Table 3 Summary of E, σ and ε of packaging films

Films	E (GPa)	σ (MPa)	ε (%)
CsDAS	0.34 ± 0.08	17.6 ± 1.3	27.0 ± 2.0
CsDAS1	0.41 ± 1.11	20.1 ± 1.1	26.8 ± 1.2
CsDAS3	0.48 ± 0.09	23.2 ± 1.2	25.4 ± 1.5
CsDAS5	0.51 ± 0.08	27.6 ± 1.1	23.0 ± 1.3

3.7. Antioxidant activities of hydrogel packaging films

The antioxidant activities of the CsDAS hydrogel packaging films were investigated in terms of total phenolic content (TPC) and DPPH radical scavenging assays, and are illustrated in Fig. 6A and B respectively. As witnessed from Fig. 6A, the TPC value increased when 1% *C. papaya* peel extract was added to the CsDAS hydrogel. An increase in PPE amount further led to an increase in TPC values. While it accounted to 1.47 µg GAE per g for pristine CsDAS, the TPC was estimated to be 2.55 µg GAE per g for the CsDAS5 hydrogel film. This behaviour could be attributed to the wide variety of phytochemicals present in PPE (as observed from the GC-MS data in Table 1), which contribute to the antioxidant activity. A high presence of antioxidants in such films will be advantageous in reducing the food oxidation and, subsequently, the deterioration.

The antioxidant capacity is suggested by the inhibition of DPPH radicals. From the results depicted in Fig. 6B; the control film (CsDAS) also showed radical scavenging activity as noted

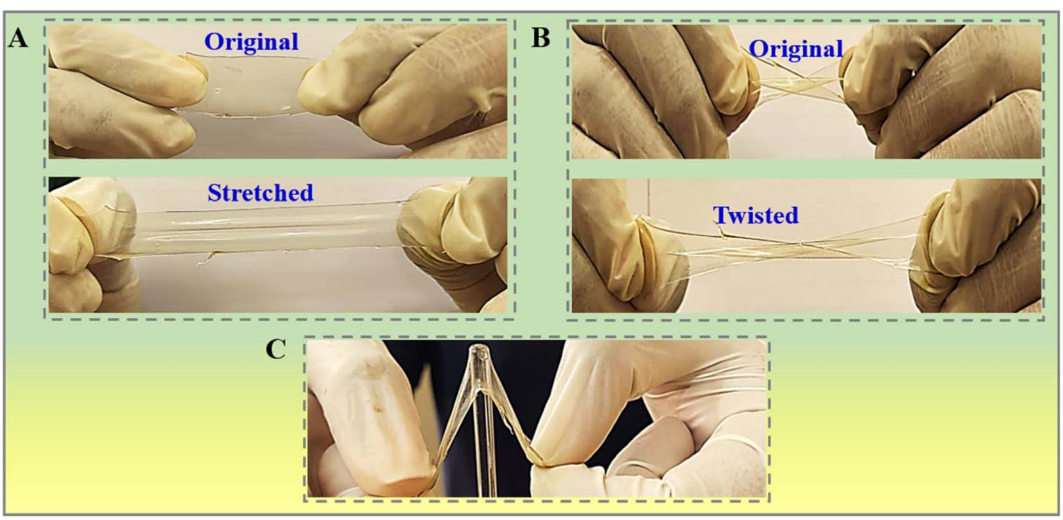


Fig. 4 Photographs of (A) stretched, (B) twisted flexibility and (C) anti-puncture resistance of chitosan-dialdehyde starch films incorporated with 5% *C. papaya* peel extract (CsDAS5).

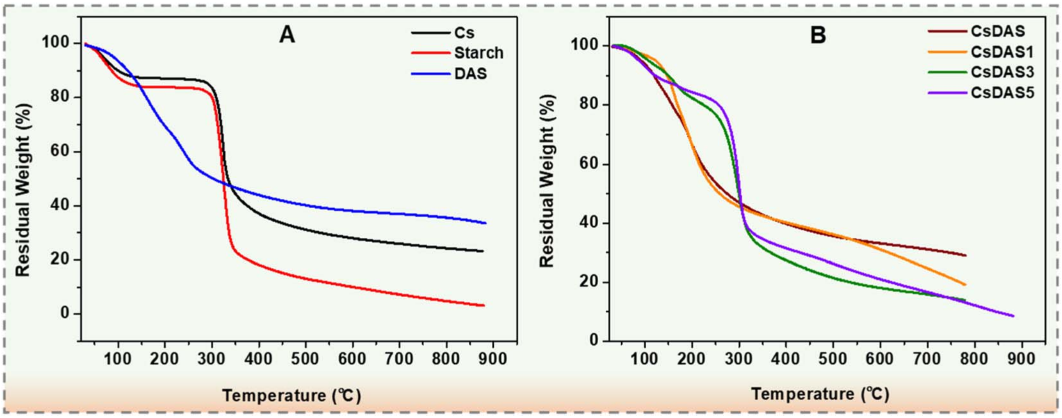


Fig. 5 TG curves of (A) chitosan (Cs), starch, dialdehyde starch (DAS) and (B) chitosan-dialdehyde starch (CsDAS) film, and *C. papaya* peel extract incorporated films at 1% (CsDAS1), 3% (CsDAS3), and 5% (CsDAS5).

from its DPPH value, which might be ascribed to the inherent property of Cs and DAS. The hydrogel films incorporated with the *C. papaya* peel extract demonstrated higher antioxidant activity in comparison to the control, the CsDAS5 hydrogel being the optimal of the lot. The report by Hanani and team showed that the addition of *C. papaya* peel extract improved the DPPH value, as the presence of antioxidants in the films led to the acceptance of electrons and/or H-atoms.[25] Thus, the incorporation of higher amounts of extract endowed the films with the desirable antioxidant activity and validated the CsDAS5 hydrogel as an apt candidate in packaging applications.

3.8. Antimicrobial activities of hydrogel packaging films

The antimicrobial activity for packaging is much an essential criterion in preventing pathogenic infections in food. Thus, the antimicrobial property of the CsDAS packaging films was evaluated. *E. coli* and *M. luteus* were chosen for this purpose. The inhibitory effects of the fabricated films on the growth of the microorganisms are presented in Table 4. Amoxicillin served as the positive control here. As witnessed, the CsDAS5 film had significant antimicrobial properties as compared to the pristine CsDAS film. The zone formed by CsDAS5 against *E. coli* and *M. luteus* bacteria was 16 and 24 mm respectively (Fig. S1 in ESI†). Recent studies have demonstrated that the bioactive components in natural extracts can damage the bacterial cell membranes leading to their inhibition.[17,31] These data recommend the efficacy of CsDAS5 as the potential packaging system.

3.9. Application of hydrogels for packaging and preservation of berries

3.9.1. Application in packaging of strawberries. Strawberry is an economically important berry fruit and much in demand by virtue of its nutritional and health effects. Unfortunately, its highly perishable nature reduces the shelf life and subsequently offers huge postharvest losses. Moreover, the berries are largely susceptible to mechanical damages and microbial infection during their harvesting and storage. Thus, the strawberry packaging industries are in urgent need of an efficient and

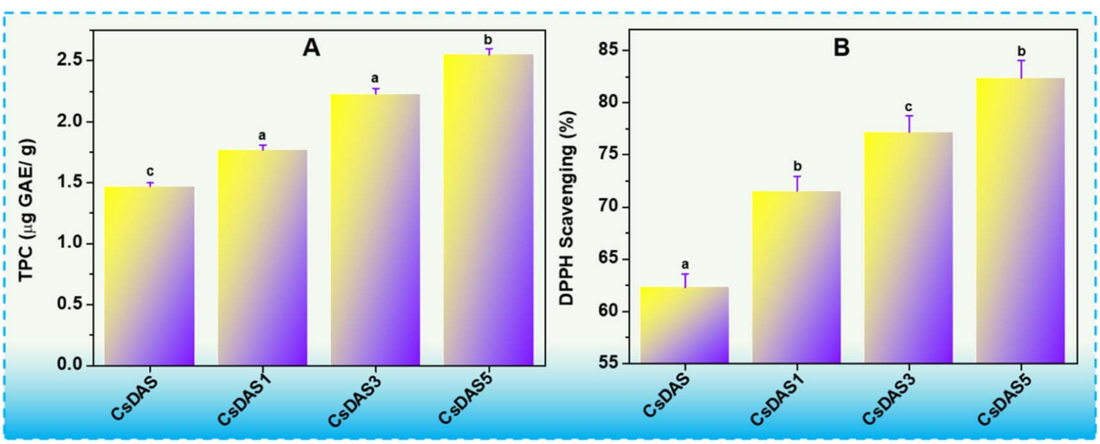


Fig. 6 Antioxidant efficacy of packaging films. (A) Total phenolic content (TPC) and (B) DPPH radical scavenging activity of the chitosan-dialdehyde starch (CsDAS) film and *C. papaya* peel extract-incorporated films at 1% (CsDAS1), 3% (CsDAS3), and 5% (CsDAS5). Letters indicate significant differences ($p < 0.05$) between the samples.

Table 4 Summary of the inhibition zones of the packaging films[a]

	Zone of inhibition (mm)	
Films	*E.coli*	*M. luteus*
CsDAS	10.05 ± 0.04^a	10.00 ± 0.11^a
CsDAS1	10.23 ± 0.00^b	20.01 ± 0.01^b
CsDAS3	12.11 ± 0.10^c	22.12 ± 0.13^c
CsDAS5	16.00 ± 0.01^d	24.00 ± 0.00^d

[a] Data expressed as mean ± SD. Different letters in the same column indicate significant differences ($p < 0.05$).

sustainable packaging and preservation system. In this work, the potential application of the developed hydrogel films as packaging systems for strawberries was determined. Fresh strawberries were packaged in different films and changes in their weight loss, decay, TA content, TSS content, and visual appearances were periodically monitored (Fig. 7 and 8).

Strawberries rot quite easily owing to their high susceptibility to the microbial invasion of their delicate skin. As depicted in Fig. 7A, the decay rate of strawberries devoid of any packaging peaked to almost 95% after 7 days. The presence of a packaging material inhibited the rot rate of the strawberries substantially. It was evident that the CsDAS5 hydrogel packaging film displayed a slower decay rate that could be attributed to the good anti-oxidation and bacterial inhibition attributes of the *C. papaya* peel extract in the film.[32]

The loss of water content in strawberries usually leads to cell aging and reduction of nutritional values. Fig. 7B reveals that the weight loss of all samples increased during the tenure. As expected, the loss in unpackaged strawberries was higher than that in the packaged ones. This could be attributed to the fact that the moisture could easily escape from unpackaged strawberries, while the packaging hydrogel films offered a hindrance in moisture loss due to their water vapour barrier property to some extent. The lowest rate was realized from the commercial polyethylene film because of its rigid and denser structure. The CsDAS5 hydrogel packaging film exhibited a lower weight loss rate than that of the CsDAS hydrogel, which could be justified to its better barrier properties.

The titratable acid (TA) content in strawberries is suggestive of their flavour which is proportional to the quantity of organic acids present in them.[55] The TA content of all groups demonstrated a continuous upward trend (Fig. 7C), which is likely attributed to the acid production by the microorganisms on the berries.[33] This observation was further corroborated from the photographs during the storage tenure (Fig. 8). In particular, the CsDAS5 hydrogel packaging film offered the lowest TA content, owing to its good antioxidant and antibacterial effects.

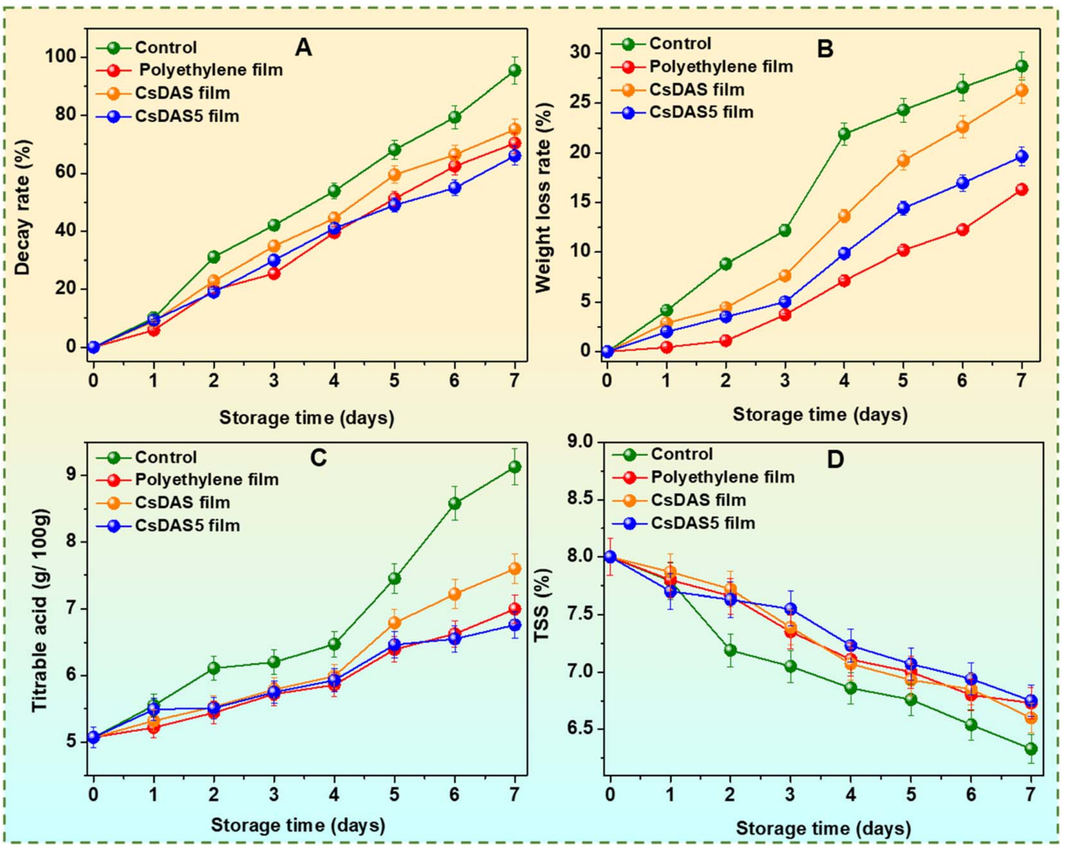


Fig. 7 Quality attributes of strawberry. (A) Fungal decay rate, (B) weight loss, (C) titratable acid (TA) content and (D) total soluble solid (TSS) content of unpackaged strawberries (control) and strawberries packaged with polyethylene, a chitosan-dialdehyde starch (CsDAS) film and a 5% *C. papaya* peel extract-incorporated film (CsDAS5) during ambient storage period.

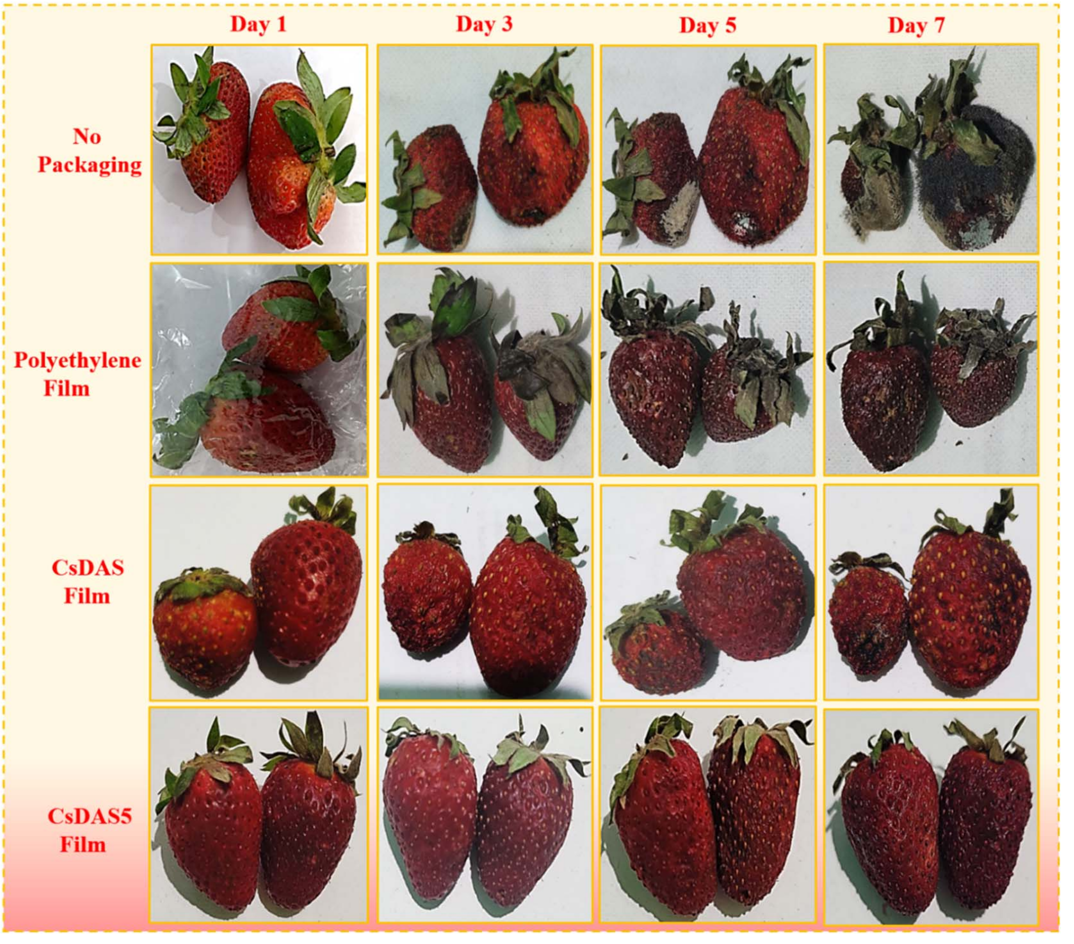


Fig. 8 Photographs of unpackaged strawberries and strawberries packaged with polyethylene, a chitosan-dialdehyde starch (CsDAS) film and a 5% *C. papaya* peel extract incorporated film (CsDAS5) during ambient storage period.

The total soluble solid (TSS) content pertains to the quality evaluation of the sweetness of strawberries.[56] Fig. 7D presents the variations in the TSS content of strawberries during experimental span. As evident, the TSS content declined for all groups, which might be due to the aging and even decay of the berries. This decrease was slower in the CsDAS5 hydrogel film group than in the CsDAS hydrogel film group, thus demonstrating its superior efficacy.

As depicted in Fig. 8, the unpackaged strawberries revealed the presence of moulds, dark coloration and evident signs of deterioration from the 3rd day onwards. Subsequently, the microbial infection gradually enhanced leading to the decay of strawberries by the 7th day. In contrast, because the CsDAS5 hydrogel packaging film was endowed with good antibacterial, antioxidant and barrier properties; the strawberries still preserved the bright red coloration and were free of molds until the 7th day. Although slight dehydration was visible, they are still acceptable for consumption. Therefore, the developed CsDAS5 hydrogel packaging film can effectually prolong the shelf life of strawberries.

3.9.2. Application in the packaging of blueberries, gooseberries and Indian jujube. Since the fabricated CsDAS5 hydrogel film demonstrated good results on strawberries, these films were further employed in the packaging of blueberries, gooseberries and Indian jujube. As illustrated in Fig. 9A, 10A and 11A; the berries packaged with the CsDAS5 hydrogel film remained afresh even after storage for 7 days under ambient conditions. However, the deterioration phenomenon could be clearly observed in the unpackaged groups. The decay rate of the unpackaged berries was much faster than that of the berries packaged with the CsDAS5 packaging film, as revealed from Fig. 9B, 10B and 11B. Further estimation of weight loss also supported the supremacy of the CsDAS5 packaging film, shown in Fig. 9C, 10C and 11C, which could be attributed to its improved barrier properties. Thus, taken altogether, it could be recommended that the multifunctional CsDAS5 hydrogel packaging film is indeed suitable for the packaging and preservation of different types of fresh berries.

3.10. Biodegradation of hydrogel packaging films

Owing to budding concerns pertaining to waste management, biodegradation of the developed packaging hydrogel films was taken into consideration in this work. The biodegradability of the CsDAS5 film was estimated by measuring its

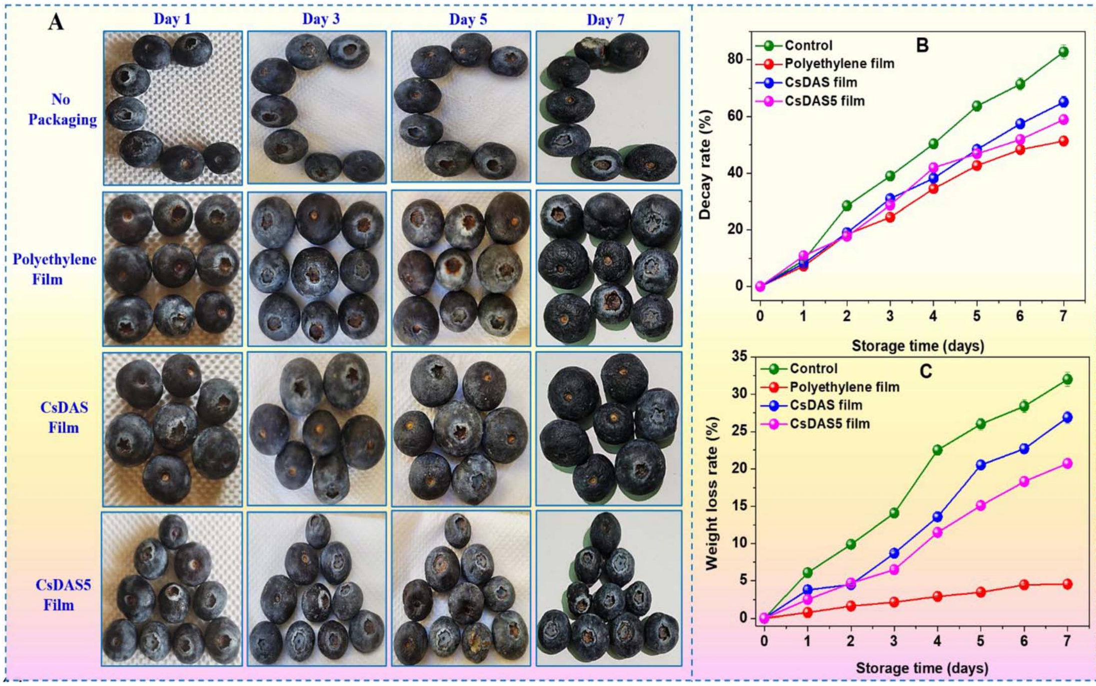


Fig. 9 (A) Visual appearance, (B) fungal decay rate and (C) weight loss of unpackaged and blueberries packaged with polyethylene, a chitosan-dialdehyde starch (CsDAS) film and a 5% *C. papaya* peel extract–incorporated film (CsDAS5) during ambient storage period.

weight loss as a function of time. Fig. 12A depicts the photographs of degradation of the films. This degradation is caused by the microbes in the soil leading to the chemical breakdown of films owing to biological stimulation. The results in Fig. 12B reveal that almost 80% of the film has underwent degradation by the 30th day. These data projected that the developed CsDAS5 packaging film is bestowed with good biodegradability.

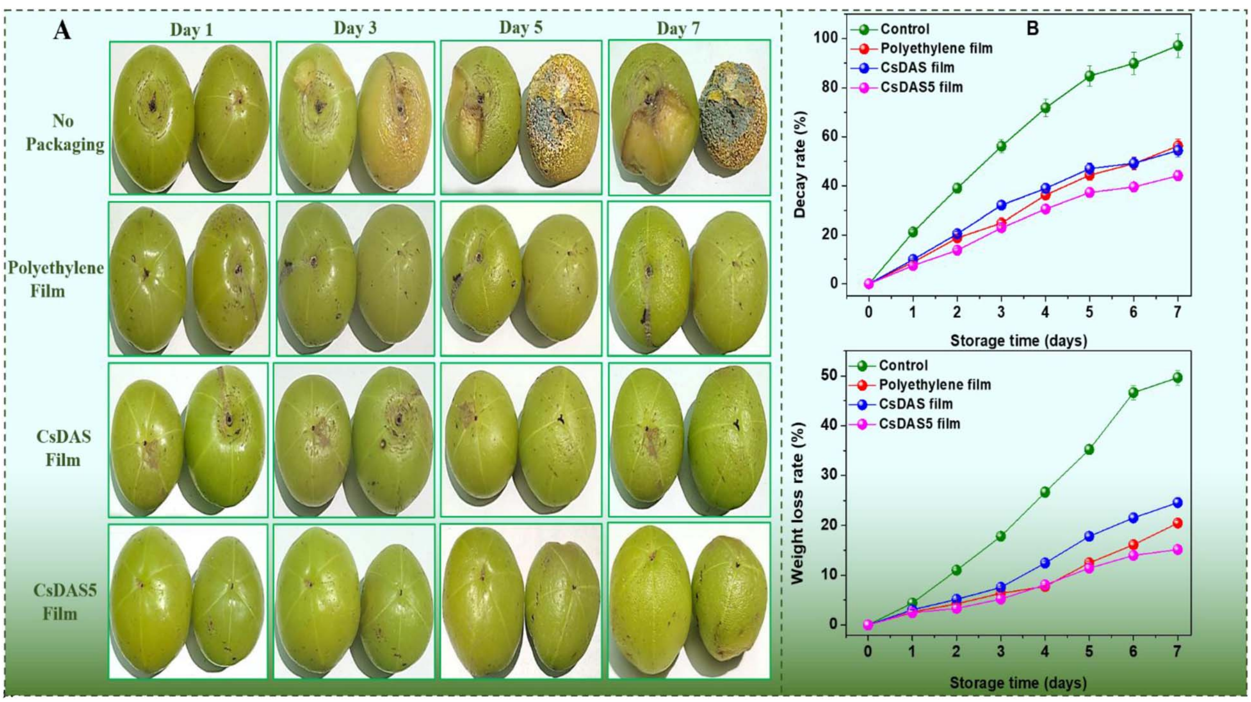


Fig. 10 (A) Visual appearance, (B) fungal decay rate and (C) weight loss of unpackaged and gooseberries packaged with polyethylene, a chitosan-dialdehyde starch (CsDAS) film and a 5% *C. papaya* peel extract-incorporated film (CsDAS5) during ambient storage period.

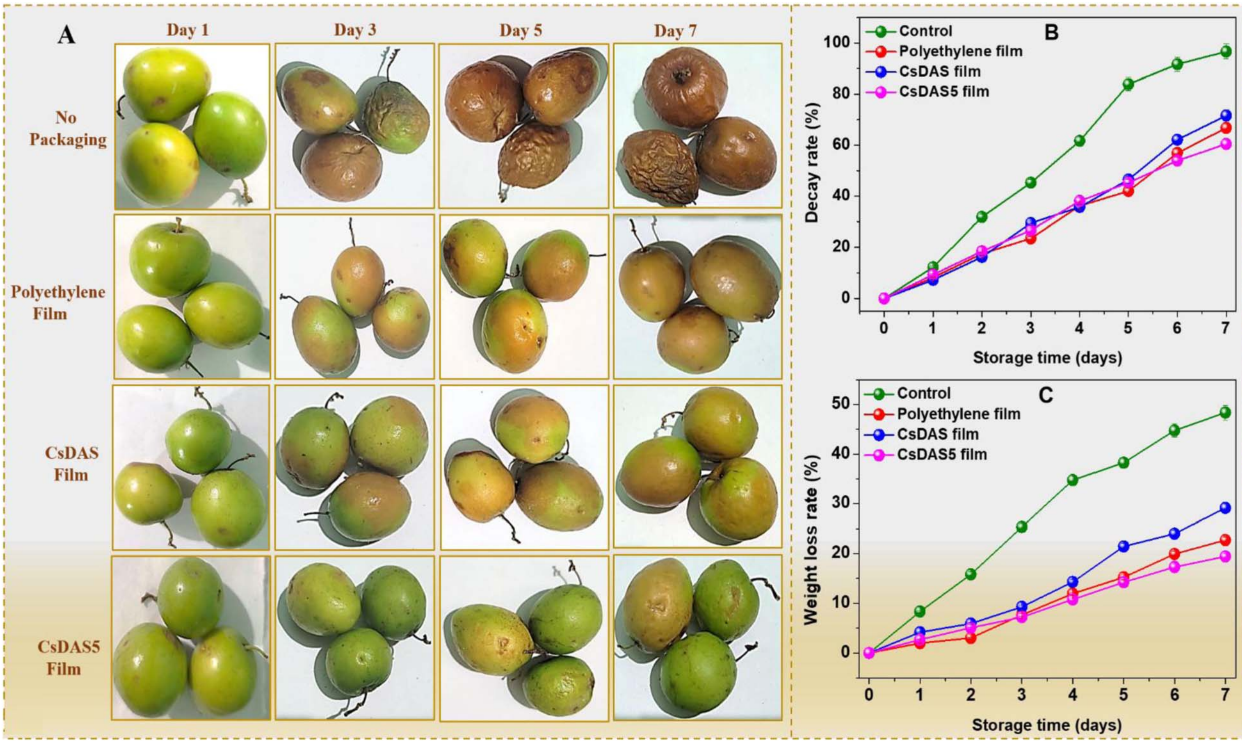


Fig. 11 (A) Visual appearance, (B) fungal decay rate and (C) weight loss of unpackaged and Indian jujube packaged with polyethylene, a chitosan-dialdehyde starch (CsDAS) film and a 5% *C. papaya* peel extract-incorporated film (CsDAS5) during ambient storage period.

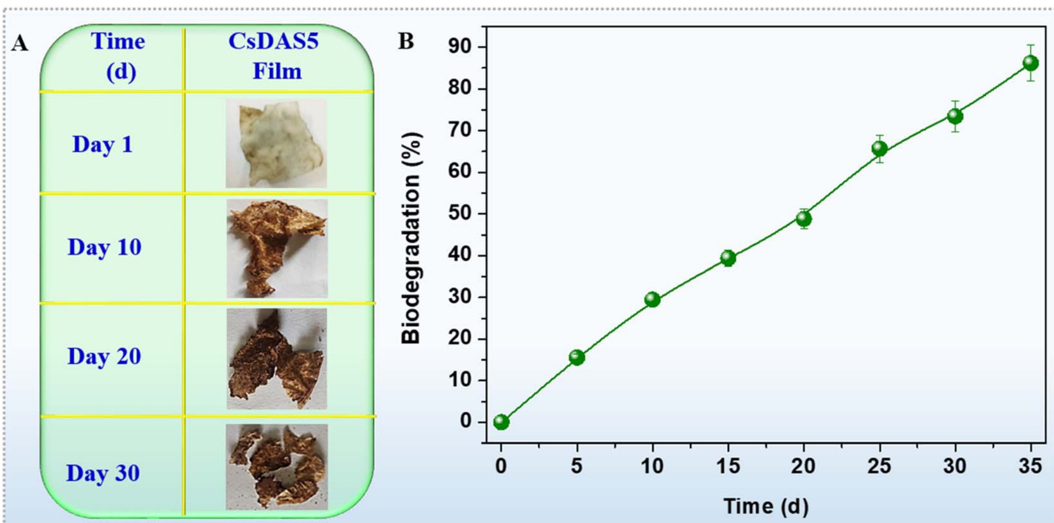


Fig. 12 Biodegradation study of the 5% *C. papaya* peel extract-incorporated chitosan-dialdehyde starch (CsDAS5) hydrogel packaging film. (A) Visual appearance of the film with gradual degradation and (B) rate of degradation in soil.

4. Conclusion

The purpose of this work was to utilize papaya peel wastes towards the design of a value-added product in the form of a packaging and preservation system for fresh berries. The film fabrication was accomplished *via* the facile strategy of *in situ* crosslinking reaction between the aldehyde groups of DAS and the amino groups of chitosan. *C. papaya* peel powders were incorporated onto the film before casting. The incorporation of *C. papaya* peel extract into the films enhanced the film thickness, moisture content and opacity. Furthermore, the fabricated CsDAS5 hydrogel film offered versatile performances in terms of antimicrobial and antioxidant activities, water-barrier properties, high tensile strength, stretched/twisted flexibility, anti-puncture resistance, thermal stability and biodegradability. The CsDAS5 film demonstrated better quality attributes for the berries and effectively prolonged their shelf-life for 7 days. In conclusion, the prepared CsDAS5 hydrogel packaging film will have tremendous application prospects in the food packaging industry.

Author contributions

GD: conceptualization, investigation, formal analysis, writing – original draft. SKD: investigation, formal analysis. SSM: investigation, formal analysis. SD: conceptualization, supervision, writing – review and editing.

Conflicts of interest

The authors declare no conflicts of interest.

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