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Original Article

Relationship between solution rheology and properties of hydroxypropyl methylcellulose films

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Abstract

The rheological properties describe flow behavior of film-forming solutions and may predict the film properties. Thus, the relationship was studied between the rheological properties and the hydroxypropyl methylcellulose (HPMC) film properties. HPMC solutions of glycerol, beeswax (BW) and stearic acid with two essential oils (EOs; ginger oil and plai oil) were measured for their steady shear responses and dynamic viscoelasticity before forming the films. The flow behavior of the HPMC solution with BW and EOs was shear-thinning non-Newtonian. Moreover, all the HPMC solutions had higher values for the loss modulus (G") than for the elastic modulus (G'). The G' and G" values of film-forming solutions with BW and EOs correlated well with the mechanical properties of the films. Furthermore, film water vapor permeability was negatively correlated with the mechanical properties of the film.

Keywords: rheological properties, hydroxypropyl methylcellulose, glycerol, beeswax, essential oil

1. Introduction

Biopolymer films and coatings can extend the shelf life and improve the quality of a food product. Films from hydroxypropyl methylcellulose (HPMC) are transparent, flexible, tasteless and odorless. The hydrophilic biopolymer HPMC makes films that are poor moisture barriers; therefore, including lipids is necessary to boost the film effectiveness as a water barrier. Beeswax (BW) is a common lipid added to HPMC edible coating on a coated paper to lessen the water vapor permeability (WVP) (Sothornvit, 2009). BW reduced the mechanical strength but enhanced the moisture barrier performance of a HPMC film (Navarro-Tarazaga, Massa, & Perez-Gago, 2011).

Generally, rheological properties describe the flow behavior of initial raw materials that finally determine food product properties. It is essential to emphasize the rheology of the film-forming solution and to relate this to the final film properties. The relationship between film composition and film properties will be useful in predicting and controlling the final film properties for food applications. Chitosan-corn starch (CH-CS) solution showed pseudoplastic (flow behavior index n<1). The CH-CS solution was thixotropic because the shear stress deformed the starch-hydrated granules that formed aggregates (Silva-Weiss, Bifani, Ihl, Sobral, & Gómez-Guillén, 2013). CH-CS with murta leave extract solution was well fit with a power law model and behaved like a dilatant fluid (n>1) at the lower shear rate of 0.4 s^{-1} but it behaved like a pseudoplastic fluid at higher shear rates. HPMC solutions with tree EO had increased k and decreased n, with pseudoplastic behavior (Sanchez-Gonzales, Vargas, Gonzalez-Martınez, Chiralt, & Chafer, 2009). Moreover, the steady-shear behavior of both HPMC types at different degrees of substitution (type E4M (DS = 1.9) and type K4M (DS = 1.4)) blended with rice flour-based batter had increased yield stress, apparent viscosity and k (Amboon, Tulyathan, & Tattiyakul, 2012). HPMC type K4M exhibited shear-thickening (n>1) flow and the complex modulus (G*) value of batter blended with HPMC increased. Moreover, storage modulus (G') was higher than loss modulus (G") (Amboon *et al.*, 2012). Recently, it was found that the flow index of a nanocomposite-forming solution decreased when the amylose content in corn starch increased, due to the interactions of the starch molecules and G' being higher than G" for all

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nanocomposite-forming solutions, which contributed to the strength of the nanocomposite films (Romero-Bastida *et al.*, 2018). Moreover, the HPMC type K4M was more easily coated on carrot slices and there was less loss of coating solution (Amboon *et al.*, 2012). Nonetheless, the rheological properties of HPMC with Thai EOs have not been investigated. As well as addressing this, the current study also investigated the film properties of HPMC with different Thai EOs and, finally, evaluated the relationship between the solution rheological properties and the biopolymer film properties.

2. Materials and Methods

2.1 Materials

Hydroxypropyl methylcellulose (HPMC; type K4M) was obtained from Dow Chemical, USA). Glycerol (Gly) and stearic acid (S) were received from Ajax Fine Chemicals Co., Ltd. (Auckland, New Zealand) and Ajax Fine Chemicals Co., Ltd. (Sydney, NSW, Australia), respectively. Beeswax (BW) was supplied from Fluka Co., Ltd. (Buchs, Germany). The ginger (G) and plai (P) essential oils (EOs) from Thai-China Flavors and Fragrances Industry Co., Ltd. (Ayutthaya, Thailand) were prepared using the steam distillation method.

2.2 Film-forming solutions

The HPMC solution (2.0% w/w) was prepared by mixing the powder thoroughly with water, heating to obtain the hydrated particles and then adding cold water (2/3 of the total water volume left) to cool down. Gly was added as a plasticizer (at HPMC to Gly ratio of 3:1 w/w) and the blend was called HPMC. The mixture of BW and S (4:1 w/w) was prepared by initially heating the BW (above 62 ºC) and the blend was called HPMC+BW/S. EO (G or P) was added to acquire 15 g/L of EO in the HPMC solution and the resultant products were called HPMC+BW/S+G and HPMC+BW/S+P, respectively. Later, a homogenizer (Polytron model PT 3100, Littau, Switzerland) at 20,000 rpm for 5 min was used to homogenize each mixture. The film-forming solutions were further used to determine their rheology properties and later to form samples of HPMC film.

2.3 Rheological properties of film-forming solutions

Steady shear and dynamic viscoelasticity flows of all film-forming solutions were tested using a controlled stress rheometer (HAAKE RheoStress 600, Thermo Electron Ltd., Germany) equipped with cone-and-plate geometry (60 mm cone diameter, 1º angle and 0.052 mm gap).

2.3.1 Steady shear measurement

All film-forming solutions were measured for their flow curves at 25 ºC and at shear rates ($\dot{\gamma}$) of 1-100 1/s. The relationship between the shear stress (σ) and $\dot{\gamma}$ was either a non-Newtonian (Bingham plastic) model ($\sigma = \sigma_0 + \eta\dot{\gamma}$) or a power law model ($\sigma = k\dot{\gamma}^n$), where η indicates the apparent viscosity (Pa.s), σ_0 indicates the yield stress (Pa), k indicates the consistency index (Pa.s^n) and n indicates the flow behavior index (dimensionless).

2.3.2 Dynamic viscoelasticity measurement

The film-forming solutions were subjected to an oscillatory stress sweep at 0-100 Pa and 1 Hz at 25 ºC to obtain the responses in linear viscoelastic range (LVR). A frequency sweep test over 0.1-100 Hz at 25 ºC was done within the LVR for each film-forming solution. Viscoelastic parameters (elastic modulus G' and loss modulus G") were determined.

2.4 Film preparation

Each HPMC film-forming solution was degassed and poured into a casting plate (21 cm × 30 cm) with a controlled total solids/plate of 10 g to reduce thickness variations between formulations. The film-forming solution was dried at 40 ºC until the film could be peeled off the plate.

2.5 Film characteristics

2.5.1 Optical properties

Color of components (BW and EOs) and all HPMC films was determined using a spectrophotometer (Spectro-guide sphere gloss, model CD-6834, BYK, Geretsried, Germany) and these are reported in the CIELAB color parameters for a 60º angle. A plastic cup (L*=31.30, a*=-2.83, b*=-2.14) and a white colored paper (L* = 90.71, a* = 0.84, b* = -4.37 and gloss = 3.7 GU) were used as a background for component and film measurement, respectively. The total color difference (ΔE*) of film compared with the HPMC film without EO was determined as shown in Equation (1).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

2.5.2 Water vapor permeability

WVP of the HPMC films was determined using a gravimetric modified cup method according to ASTM E96. Films without any defects were cut and placed airtight onto the cup with its base occupied with 7 mL distilled water. The cups were kept in a cabinet at 50 % relative humidity (RH) and 27 ± 3 ºC. When the steady-state moisture transfer was achieved, the weight was recorded in order to calculate the water vapor transmission rate (WVTR). WVP was determined as shown in Equation (2).

$$WVP = \frac{WVTR\ x\ thickness}{p_{A1} - p_{A2}} \quad (2)$$

where, p_{A1} - p_{A2} is the water vapor partial pressure difference across the film (p_{A1} is water vapor partial pressure inside the cup and p_{A2} is water vapor partial pressure outside the cup).

2.5.3 Mechanical properties

The film mechanical properties (tensile strength TS, elastic modulus EM and elongation E) were measured using a

Universal Testing Machine (Instron model 5569, MA, USA) with a 0.5 kN load cell according to ASTM standard D882-97. Dumbbell-shaped specimens (10 mm wide and 100 mm long tested area) were die-cut and preconditioned at 27 ± 2°C and 50 ± 5% RH for at least 48 h prior to the test. The 100 mm initial gauge separation and the 50 mm/min crosshead speed were set.

2.6 Statistical analyses

A completely randomized design was used to determine each property with at least three replications. SPSS 11.0 for Windows (SPSS Inc., Chicago, IL, USA) was employed for analysis of variance and Duncan's multiple range test was used to determine the significant differences between treatments ($p < 0.05$).

2.7 Relationship between rheological properties of film-forming solution and film properties

The rheological properties of film-forming solution and film properties were subjected to principal component analysis (PCA). The multivariate analysis with factor analysis was used to determine the highest significant ($p < 0.05$) data variances using SPSS 11.0 for Windows.

3. Results and Discussion

3.1. Rheological properties of film-forming solutions

3.1.1 Steady shear behavior

The relationship between σ and $\dot{\gamma}$ for the HPMC solution followed a power law model with shear-thinning behavior (n<1) (Table 1) similar to a 1-2.5% HPMC solution (Steffe, & Ford, 1985). The HPMC film-forming solution had sufficient viscosity to provide a strong network as a biomaterial film. The inclusion of BW in the HPMC solution (HPMC+BW/S) maintained the shear-thinning behavior (n<1) with no significant change in k but with a significantly increased n. This also affected the optical properties (lower L*, ΔE* and gloss values) and the mechanical properties (lower EM and higher E) of film as described later. The inclusion of G in the HPMC+BW/S solution (HPMC+BW/S+G) did not change the k and n values. However, the inclusion of P (HPMC+BW/S+P) substantially decreased the k and increased the n significantly. In contrast, adding tea tree EO in the HPMC film-forming solution significantly increased k and decreased n (Sanchez-Gonzalez, Gonzalez-Martinez, Chiralt, & Chafer, 2010). This indicates that the type of EO added into the biopolymer solution affects the flow behavior of the film-forming solution.

3.1.2 Viscoelastic behavior

The oscillatory stress sweep test displayed LVR of HPMC solution at a stress value of 1 Pa, while the LVR values for HPMC+BW/S, HPMC+BW/S+G and HPMC+BW/S+P were at 10 Pa. The LVR at 10 Pa was wider than at 1 Pa indicating a stronger gel. In addition, the frequency sweep test showed that all solutions possessed greater values of G" than G' at all frequencies, as shown in Figure 1. This indicates that the solution showed predominantly viscous behavior. The G' and G" values increased with frequency. A higher value for G" than G' meant that the solution required higher energy to deform. The film-forming solution behaved as a liquid-like material (Tabilo-Munizaga, & Barbosa-Cánovas, 2005). This corresponds to a higher G" than G' for spray-dried reconstituted mucilage (León-Martínez *et al.*, 2011).

Table 1. Consistency index (k) and flow behavior index (n) of HPMC-based film-forming solution prepared with glycerol (Gly), beeswax (BW) and ginger oil (G) or plai oil (P) with coefficient of determination (r^2) for the power law model fit.

Sample	k (Pa.s)	n	r^2
HPMC	6.0275 ± 0.1656 [b]	0.6833 ± 0.0068 [a]	0.9925
HPMC+BW/S	5.8945 ± 0.4943 [b]	0.6988 ± 0.0004 [b]	0.9918
HPMC+BW/S+G	5.7790 ± 0.0898 [b]	0.7040 ± 0.0028 [b]	0.9903
HPMC+BW/S+P	2.5698 ± 0.0548 [a]	0.7995 ± 0.0007 [c]	0.9945

Values are averages of three replicates ± standard deviation.
Different letters indicate that the averages within the same column are different at the 0.05 level of significance.

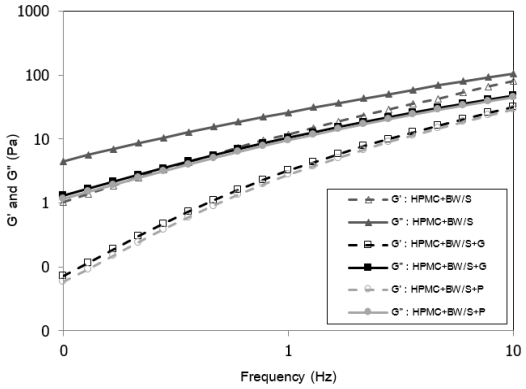

Figure 1. Elastic modulus (G') and loss modulus (G") of HPMC+BW/S, HPMC+BW/S+G and HPMC+BW/S+P at 10 Pa

3.2 HPMC-based film characteristics

3.2.1 Optical properties

Color is a key factor affecting consumer acceptability and EO might influence the film optical properties. The main color parameters (L*, a* and b*) of components such as BW and EOs themselves were as follows: L*=60.31±0.77, a*=-2.60±0.38, b*=13.83±0.55 for BW; L*=30.67±0.04, a*=1.60±0.06 b*=17.20±0.17 for G; and L*=33.53±0.16, a*=-1.12±0.07, b*=7.56±0.11 for P. As seen, BW and EOs showed lower L* values, and a* and b* depended on the nature of each component. As reflected in film, BW decreased the L*, a* and gloss values but increased the b* value in HPMC+BW/S film (Figure 2) corresponding to subjective visual appearance. The degree of total color difference (ΔE*) of the film was higher when BW and EO were added. This might be due to the oxidation reaction between EO and oxygen during film formation. A similar result was reported with ΔE* of hake protein film increasing

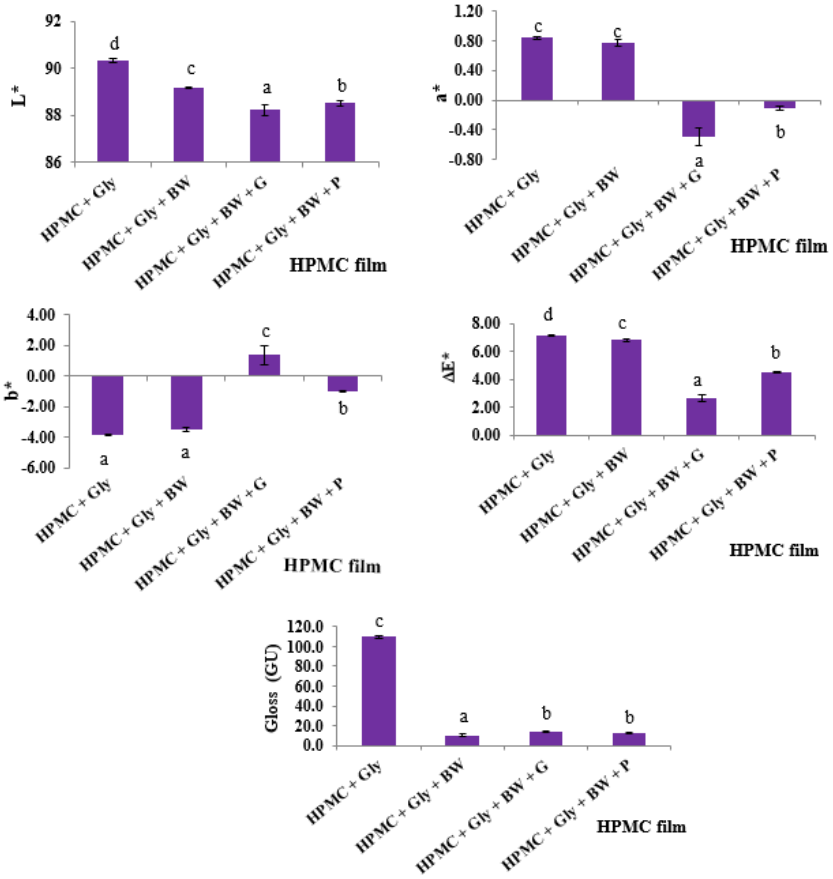

Figure 2. Effect of essential oil type (ginger, G and plai, P) on color (L*, a*, b*) total color difference (ΔE*) and gloss of HPMC-based composite films. Error bars show standard deviations. Different letters indicate that the averages are different at the 0.05 level of significance.

with tarragon and coriander oils (Pires *et al.*, 2013). Moreover, the essential oils significantly decreased the gloss of the HPMC+BW/S+G and HPMC+BW/S+P films. Likewise, HPMC film with tea tree oil had decreased gloss and transparency depending on the oil content used (Sanchez-Gonzalez *et al.*, 2009). Furthermore, the opaqueness and color intensity of alginate film with added garlic oil were higher than for film without the oil, which was more transparent (Pranoto**,** Rakshit, & Salokhe, 2005). However, phayom wood extract added into HPMC films made the color lighter and red-yellowish (higher L*, a* and b* values) when phayom wood extract content was increased (Jutaporn, Suphitchaya, & Thawien, 2011). Chitosan-based films with cinnamon oil had noticeably higher ΔE*, while films with thyme and clove oil were not affected (Hosseini, Razavi, & Mousavi, 2009). Nevertheless, the inclusion of ginger oil did not change the color parameters of gelatin films (Ahmad, Benjakul, Prodpran, & Agustini, 2012). The reduction of gloss might be attributed to the surface roughness and chemical heterogeneity (Trezza, & Krochta, 2001) including the hydrophilic/hydrophobic properties of the film components (Sothornvit, 2009). Therefore, the current results imply that the type of EO was a factor affecting the film color. Even though the EO provided an intensive optical effect, the yellowish color of film might be advantageous as it can protect against light and retard the oxidation of food products.

3.2.2 Water vapor permeability

Generally, EO or a lipid with hydrophobic properties could reduce the film WVP. In the current study, the BW did not lower WVP of the HPMC films (Figure 3). This might have been due to the small amount of BW used, and it did not show any water barrier improvement. However, the EO significantly reduced the film WVP, compared with HPMC+BW/S film. This was attributed to the hydrophobicity of the essential oils. Similarly, in HPMC film a tea tree oil decreased the film WVP (Sanchez-Gonzalez *et al.*, 2009). However, no changes in the WVP were observed in alginate-apple puree films with oregano, carvacrol, lemongrass, citral or cinnamon oils (Rojas-Grau *et al.*, 2007) or in a sodium caseinate-based film with cinnamon or ginger oils (Atares, Perez-Masia, & Chiralt, 2011). Moreover, G reduced film WVP less than P. The plai oil might act as a plasticizer superior to ginger oil and decrease the intermolecular interactions (Pranoto *et al.*, 2005). Then the moisture could more easily diffuse through the film so that WVP of the HPMC+BW/S+P film was increased.

3.2.3 Mechanical properties

The inclusion of BW (HPMC+BW/S) decreased the film EM and increased E significantly but the TS was not

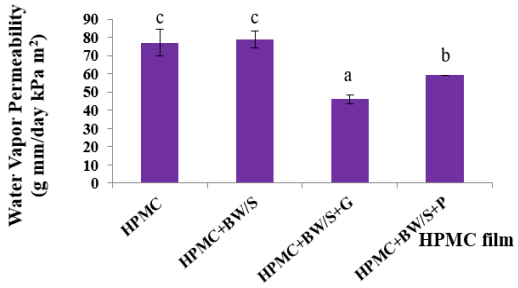

Figure 3. Effect of essential oil type (ginger, G and plai, P) on water vapor permeability of HPMC-based composite films. Error bars shows standard deviations. Different letters indicate that the averages are different at the 0.05 level of significance.

significantly affected, compared to the HPMC film. Generally, the lipid globules disperse in the film network and loosen the film strength compared to the film without lipid (Gontard, Marchesseau, Cuq, & Guilbert, 1995). Moreover, certain lipids might be heterogeneous in film-forming solution and might lower the strength of such films. It could be that BW acted as a plasticizer, similarly to Gly. However, the incorporation of the EO significantly affected the mechanical properties. The inclusion of EO significantly decreased TS and EM but increased E in the HPMC+BW/S+G and HPMC+BW/S+P films compared to the control (HPMC) film or to HPMC+BW/S film (Table 2). The EO also acted as a plasticizer resulting in a lower strength of HPMC film. However, there was no significant difference in mechanical properties among the different EOs used, except a higher E of HPMC+BW/S+G films than of HPMC+BW/S+P films. This might be due to the significant differences in flow behavior of different EOs as mentioned previously. Thus, the unique chemical composition and structure of G possibly caused it to interact less with the HPMC polymers, resulting in higher E values for the HPMC+BW/S+G films. Generally, the presence of EO loosened the film network of the polymer-oil interactions and hence has been reported to lower the strength of alginate-apple puree film containing oregano, carvacrol, cinnamon or lemongrass oil (Rojas-Grau *et al.*, 2007), HPMC film with tea tree oil (Sanchez-Gonzalez *et al.*, 2009), emulsified chitosan-based films (Sanchez-Gonzalez *et al.*, 2010), oregano EO (*Origanum Vulgare* L.) incorporated in soybean polysaccharide films (Liu *et al.*, 2019) and sodium alginate based active edible films with EOs from *R. officinalis* L., *A. herba alba* Asso, *O. basilicum* L. and *M. pulegium* L. (Mahcene *et al.*, 2020). Moreover, the TS of alginate film with garlic oil was reduced because garlic oil blocked the ionic bonds between the alginate and calcium ions of the polymer structure (Pranoto *et al.*, 2005).

3.3 Relationship between rheological properties and film properties

The rheological property data on G' and G" were used to evaluate their relationship with the film properties TS, EM, E and WVP. All these variables were subjected to PCA excluding the film color parameters that were not relevant to the rheological properties. The number of principal components was regulated by the eigenvalues. The PCA

Table 2. Tensile strength (TS), elastic modulus (EM) and elongation (E) of HPMC-based film-forming solution incorporated with glycerol (Gly), beeswax (BW) and ginger oil (G) or plai oil (P).

Sample	TS (MPa)	EM (MPa)	E (%)
HPMC	21.70 ± 0.89 [b]	74.07 ± 20.11 [c]	45.03 ± 1.44 [a]
HPMC+BW/S	19.58 ± 1.99 [b]	42.34 ± 4.55 [b]	63.56 ± 1.51 [c]
HPMC+BW/S+G	9.37 ± 0.36 [a]	6.97 ± 0.37 [a]	58.78 ± 2.38 [b]
HPMC+BW/S+P	8.74 ± 1.30 [a]	13.87 ± 1.47 [a]	41.17 ± 3.73 [a]

Values are averages of three replicates ± standard deviation.
Different letters indicate that the averages within the same column are different at the 0.05 level of significance.

indicated that the rheological properties correlated with the film properties (Figure 4). The number of components and the variance for the rheological properties with regard to the film properties were 3 and 100 %, respectively. The G' value of film-forming solution with BW and EOs correlated well with the mechanical properties of the film. The inclusion of BW showed that the initial G' was related to the EM and TS of the film. Furthermore, the film WVP was adversely correlated with the mechanical properties of the film. When the essential oil G was included in the HPMC film, the initial G' value of the film-forming solution reflected the TS and EM of the film. Multivariate analysis techniques could identify which rheological parameters of the film-forming solution were correlated with the film properties. Therefore, the compositions related to the rheological properties can be used to tailor the film properties for a specific final food application.

4. Conclusions

The flow behavior of HPMC solution with BW and EOs was well represented by a shear-thinning model (n<1) and had liquid-like behavior (G">G') with suitable viscosity for film formation. Interestingly, the inclusion of BW and EOs

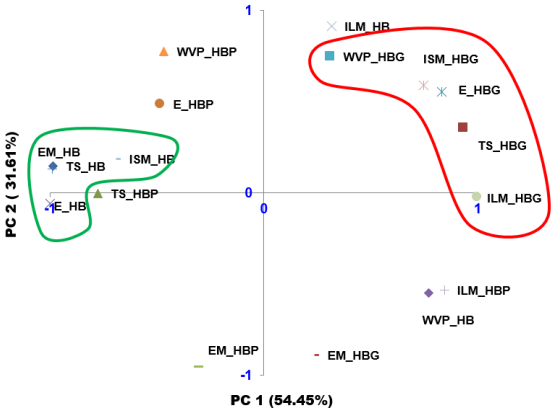

Figure 4. Loading plots of rheological properties of film-forming compositions and properties of HPMC-based composite films prepared with beeswax (BW) and essential oils of various types (ginger, G and plai, P). Note: I = initial, SM = storage modulus, LM = loss modulus, WVP = water vapor permeability, TS = tensile strength, EM = elastic modulus, E = elongation, HB = HPMC+BW/S, HBG = HPMC+BW/S+G and HBP = HPMC+BW/S+P

in the HPMC films significantly altered the physical film appearance, WVP and mechanical properties compared to the HPMC films (control). The relationship between rheological properties and film properties was determined using factor analysis based on principal component analysis. The inclusion of BW and EOs lowered the G' and G" values and correlated with a reduction of film properties. Therefore, the rheological property parameters of film-forming solution can be used to tailor the HPMC film properties.

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