Optimization of amount of amylose, methylcellulose and hydroxypropylmethylcellulose for maximum tensile strength and minimum water vapour permeability of corn starch based self-supporting films

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Corn starch based self-supporting film has been developed from a fixed quantity of polymer that contains corn starch and functional polysaccharide such as amylose, methylcellulose and hydroxypropylmethylcellulose. The optimum amount of functional polysaccharide in order to obtain maximum tensile strength and minimum water vapour permeability of film has been determined. It is observed that increasing addition of functional polysaccharide (amylose/methylcellulose/hydroxypropylmethylcellulose) in blend increases the tensile strength of film to a maximum value, following a decreasing tendency with further addition. The trend for water vapour permeability is found to be opposite. The concentration of functional polysaccharide at the inflection point of maximum tensile strength and minimum water vapour permeability does not always match, thus necessitating the need of optimization. Response surface methodology using design expert numerical optimization could successfully predict the optimum value of functional polysaccharide in starch blend to attain maximum tensile strength and minimum water vapour permeability of developed film. For amylose, methylcellulose, and hydroxypropylmethylcellulose, the optimized levels are found as 0.65, 0.10, and 0.22% in case of glycerol–water plasticizer, and 0.74, 0.08, 0.29% in case of glycerol-polyethylene glycol-water plasticizer respectively.

Keywords: Corn starch, Functional polysaccharide, Functional properties, Plasticizer, Self-supporting film, Starch film

Self-supporting films (SSF), a stand alone thin layer of materials such as polysaccharides, proteins, and plasticizers, can form instant soluble pouches that get dispersed into cooking medium along with its contents. Such pouches can preserve the inherent aroma of foods, when kept in a secondary package to protect from aerial humidity. Undoubtedly, these applications can partially reduce the use of synthetic plastic. However, for successful implementation, the films must possess appropriate mechanical, barrier, and other properties that can be moderated with proper selection of polymers and plasticizers including glycerol, xylitol, sorbitol and polyethylene glycol. Plasticizers moderate the intermolecular linkages. Among the food grade polymers, the use of starch is of great interest since this is abundant, cheap and renewable. Recently starch based films are particularly being considered for their desirable physical characteristics like being transparent, odourless, tasteless, semi-permeable to CO₂ and resistant to O₂ passage. Starch contains both linear amylose and branched amyllopectin. Being a straight chain carbohydrate, amylose (AM) develops a close matrix by inter-linkage with adjacent chains and thereby results in strong flexible film, but the presence of branches in amyllopectin therein affects the matrix development by AM; as a result, starch films ultimately show poor mechanical and water vapour barrier properties. For this, high-AM starch is a better option. According to Garcia et al., degree of crystallinity of film increases with increasing AM content of starch, and more the microcrystalline domain appears the higher is its tensile strength. However, Rindlav-Westling et al. and Paes et al. reported that in spite of the presence of native AM in starch, incorporation of additional AM acts as functional polysaccharide that improves the crystalline character of blend film. Though few references are available on starch-protein and starch-lipid blends, no report on mechanical and other properties of such starch-AM blend film is available.

Derivatives of cellulose like methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC)
have excellent film forming capability. The chains of these derivatives remain associated by hydrophobic force among the hydrophobic groups in substituted and hydrophilic force among the un-substituted regions, thereby producing desirable characteristics in the film. Shi and BeMiller stated that when hydrocolloids (cellulose derivatives, gums, etc.) are mixed with starch and gelatinized, leached AM and low molecular weight amylopectins can interact with hydrocolloids and form different network structures that result in altered rheological properties depending on the hydrocolloid and its concentration. According to Arvanitoyannis et al. and Tao et al., poor physical properties of starch film/composite can be improved by blending with functional ingredients like cellulose derivatives and proteins. Psmiadiou et al. and Arvanitoyannis and Biliaderis measured the thermal, mechanical and permeability properties of films made from blends of presolubilised-roller dried starch plus MC using different combinations of glycerol, sugar and water as plasticizers. However, literature on native starch-MC blend film is limited. Though in pharmaceutical and food aspects, the benefits of the interaction of starch and HPMC are being utilized, report on films from such blends is scarce. Very recently, the influence of HPMC in corn starch based film on structural, optical, tensile and barrier properties was analyzed by Jimenez et al.

As phase separation is common in solution of different biopolymers, it is important to know about their miscibility when blending of two or more polymers is aimed. The nature of biopolymers, their concentrations, temperature, and other conditions of film preparation determine this behaviour. In blended amylose and amylopectin films, Wolff et al. and Lourdin et al. observed that the mechanical properties show increasing elongation and strength with an increasing amount of AM, while Rindlav-Westling et al. reported a dramatic increase in the crystallinity for only up to a proportion of 25% AM. Turhan and Sahbaz stated that at high concentration, MC shows partial insolubility in films plasticized with polyethylene glycol resulting in decrease of mechanical properties. Phase separation may result in poor mechanical properties of films from a blend of polymers, therefore mixing in optimum ratio must be resorted to for best result.

In the present work films have been developed from a fixed quantity of polymer that contains variable amount of corn starch and complementary amount of a functional polysaccharide (FP) like AM, MC, and HPMC. The objective is to determine, using response surface methodology, the optimal amount of the FP in blend that provided maximum tensile strength and minimum WVP (water vapour permeability) of the developed films.

**Experimental Procedure**

**Ingredients for film making**

Commercial grade white free flowing corn starch powder (ANGEL, LK18, Angel Starch and Chemicals Pvt. Ltd., Tamil Nadu, India; detailed composition in Table 1) was procured in a lot of 50 kg and used as the basic raw material. Potato AM (Sigma Chemical Company, USA), MC (methoxy content 28-32%, Loba Chemie Pvt. Ltd., Mumbai, India) and HPMC (Hi Media Pvt. Ltd., India) were used as the FP(s). Since the presence of gelatin in film formulation may lead to formation of triple helix structure of native collagen that act as ‘initiators’ for the development of a three-dimensional network, a fixed amount of gelatin (Loba Chemie Pvt. Ltd., Mumbai, India) was added in all the blends containing MC. Glycerol (Gly, 87%, AR) and polyethylene glycol 400 (PEG, AR), both procured from Merck Specialties Pvt. Ltd., Mumbai, India, and glass distilled water in two different combinations, viz. Gly-water (binary system) and Gly-PEG-water (ternary system) were used as plasticizers. All the ingredients added in blends have been expressed as per cent (%), weight (w)/weight (w) of blend [(calculated as weight of ingredient/weight of blend) × 100].

**Experimental design**

Experiment was designed to obtain different amounts of FPs (AM/MC/HPMC) as independent variable to be added to corn starch in three combinations. The objective is to determine, using response surface methodology, the optimal amount of the FP in blend that provided maximum tensile strength and minimum WVP (water vapour permeability) of the developed films.

### Table 1—Composition of corn starch used for film preparation

<table>
<thead>
<tr>
<th>Components</th>
<th>Tested value* %, wt basis</th>
<th>Reported value %, wt basis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>13.46</td>
<td>13</td>
<td>47</td>
</tr>
<tr>
<td>Amylose</td>
<td>21.70</td>
<td>16.9-21.3</td>
<td>48</td>
</tr>
<tr>
<td>Protein</td>
<td>0.35 (Nitrogen×6.25)</td>
<td>0.31</td>
<td>49</td>
</tr>
<tr>
<td>Fat</td>
<td>0.04</td>
<td>0.12</td>
<td>50</td>
</tr>
<tr>
<td>Ash</td>
<td>0.02 (550°C for 4h)</td>
<td>0.05</td>
<td>50, 51</td>
</tr>
</tbody>
</table>

*Composition of procured starch was analysed following standard methods.
polysaccharide blends (starch-AM, starch-MC, and starch-HPMC) for preparing films, while the dependent variables or responses considered were film’s tensile strength and WVP. One–factor, cubic model, response surface methodology (Design Expert 7.0, Stat Ease, Inc., USA) was used for this purpose. The lowest and highest permissible limits in real values, selected from preliminary trial experiments, varied 0-1.16% and 0-0.17% for AM and MC respectively, for both binary and ternary plasticized films. However, the limits for HPMC in starch-HPMC blend were dependent on the plasticizer type, i.e. 0-0.38% for binary and 0-0.58% for ternary systems. The selected model generated coded values of each FP as central point 0, maximum +1, minimum -1, and interior points as -0.666, -0.333, +0.666, and +0.333. The design of experiment indicated 10 experimental runs including two runs for each of the central, maximum and minimum points and one run for each of the interior points. Detailed experimental plan with real and coded values is shown in Table 2.

### Preparation of blend and casting of film

Blends were prepared using 6 g total polymer that contained corn starch, AM, MC, HPMC and gelatin, in various combinations as explained hereunder. For maintaining the polymer content at 6 g, the amount of starch was compensated with the other polymer(s) used. Binary plasticizer system included Gly (2 mL)–water (78 mL), while ternary system contained Gly (1.46 mL)–PEG (1 mL)–water (77.54 mL), total liquid being 80 mL in each blend. For preparation of blends, a similar technique for dissolution of polymer was followed, irrespective of binary and ternary system of plasticizers.

For AM containing blends, AM was dissolved in 30 mL portion of water taken in a 250 mL conical flask by swirling. Required amount of corn starch and remaining plasticizers [polyol(s) and rest of water] for the respective system were added to the preformed amylose solution and mixed well manually with spatula.

For MC containing blends, MC was soaked in 30 mL portion of water in a 250 mL conical flask for overnight. The mixture was heated in boiling

### Table 2 — Real and coded values of each functional polysaccharide (independent variable) obtained by one factor, cubic model experimental design for different blends using binary and ternary plasticizers

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Experimental runs</th>
<th>AM in starch-AM blend*</th>
<th>MC in starch-MC blend†</th>
<th>HPMC in starch-HPMC blend*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary plasticizer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2.85% Gly + 90.21% water)</td>
<td>1</td>
<td>0.97 (+0.666)</td>
<td>0.14 (+0.666)</td>
<td>0.12 (-0.333)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.16 (+1)</td>
<td>0.11 (+0.333)</td>
<td>0 (-1)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.16 (+1)</td>
<td>0 (-1)</td>
<td>0.17 (0)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.58 (0)</td>
<td>0.17 (+1)</td>
<td>0.06 (-0.666)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.19 (-0.666)</td>
<td>0 (-1)</td>
<td>0.23 (+0.333)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.39 (-0.333)</td>
<td>0.09 (0)</td>
<td>0.17 (0)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.58 (0)</td>
<td>0.17 (+1)</td>
<td>0.35 (+1)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.00 (-1)</td>
<td>0.03 (-0.666)</td>
<td>0.35 (+1)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.00 (-1)</td>
<td>0.09 (0)</td>
<td>0 (-1)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.77 (+0.333)</td>
<td>0.06 (-0.333)</td>
<td>0.29 (+0.666)</td>
</tr>
<tr>
<td><strong>Ternary plasticizer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2.08% Gly + 1.31% PEG + 89.67% water)</td>
<td>1</td>
<td>0.19 (-0.666)</td>
<td>0.17 (+1)</td>
<td>0.29 (0)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.16 (+1)</td>
<td>0.06 (-0.333)</td>
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<td>0.20 (-0.333)</td>
</tr>
</tbody>
</table>

*Values in parentheses are coded values.
**Starch plus AM/HPMC in blend was 6.94%.
†Blend containing 1.16% gelatin and 5.78% of starch plus MC, total polymer being 6.94%.
water bath for 10 min in order to obtain clear solution that was naturally cooled to room temperature. As the MC containing films also contained gelatin, 1 g gelatin was dissolved separately in another 30 mL portion of water taken in a 250 mL conical flask by stirring with a spatula. Required amount of corn starch was added in the gelatin solution. The content was transferred quantitatively by washing with water to the MC solution; the remaining plasticizers were added and mixed well.

For HPMC containing blends, HPMC was soaked overnight in a 250 mL conical flask with 30 mL of water. The solution was then heated in a boiling water bath until clear solution was obtained. In a 250 mL beaker the required amount of corn starch was dispersed with another 30 mL of distilled water and then the starch solution was poured quantitatively into the HPMC solution and stirred well with spatula. The rest of the plasticizers were added and mixed well.

Preparation of respective control blends (without FP) was done similarly, except the prior dissolution of AM, MC and HPMC as mentioned above. Composition of the blends in per cent (w/w of blend) is indicated in Table 2. The blend was gelatinized, cast with a thin layer chromatography applicator, dried and the developed film was stored as described elsewhere\(^5\). For each composition 10-12 films were cast.

Measurement of properties

Prior to measurement of properties such as tensile strength and water vapour permeability (WVP), films were cut in specific shape and conditioned\(^5\) at 50% RH at 25°C for at least 48 h.

Tensile strength was estimated according to ASTM D882-97 using Instron Universal Testing Machine (model 1011; Instron Corp., Canton, MA, USA). The cut film having a dimension of 100 mm gauge length (with 10 mm for gripping at both ends) and breadth of 10 mm was used for the testing. Films were cut both vertically (along the web) and horizontally (perpendicular to the web), 5 replications each. Thickness of each conditioned film piece was determined as per ASTM E96-80 by gravimetric method\(^2,54,57-61\). A perspex cup having 4.0 cm inner diameter, 1.9 cm height, and provided with a collar type lid and rubber washer, both of 4.0 cm diameter, was used for measurement. The cup was filled with distilled water occupying \(\approx 50\%\) of its volume. The test film cut in the form of circular disc (diameter 5.0 cm), after measuring the thickness as indicated above, was placed leak proof at the mouth of the cup covering the aperture. This maintained 100% RH inside the cup. The rubber washer was then placed on the film followed by fixing the collar lid on it with the help of four screws 90\(^\circ\) apart. The cup was then placed in a desiccator maintained at 50% RH using saturated solution of sodium dichromate. The desiccator was kept at 25±1°C inside an incubator. Thus, a fixed RH gradient of 100 % and 50% was maintained across the film surface. Initial weight of the cup (\(W_1\) g) and the final weight (\(W_2\), g) after 24 h were recorded, and WVP value was calculated using the following equation:

\[
WVP(g.mm/kPa.m^2.h) = \frac{(W_1-W_2)h}{(P_{A1}-P_{A2})A_1T_1} \quad \cdots (1)
\]

where \(h\) is the film thickness (mm); \(P_{A1}\) and \(P_{A2}\), the partial pressures (kPa) of water vapour at 100% and 50% RH respectively; \(A_1\), the area of the exposed film (m\(^2\)); and \(T_1\), the time (h) during which the change in weight has taken place. The measurement was done in three replications for each film composition.

Regression analysis

The correlation between the independent (amount of FP) and the dependent parameters (tensile strength and WVP) were obtained following non-linear regression technique using the software Design Expert 7.0. Initially, third order polynomial response surface models were fitted to relate respective response ‘\(Y\)’ and corresponding independent variable ‘\(X\)’ according to the following equation:

\[
Y = B_0 + B_1X + B_2X^2 + B_3X^3 \quad \cdots (2)
\]

where \(B_0\), \(B_1\), \(B_2\) and \(B_3\) represent the estimated regression coefficients with \(B_0\) as the constant term; \(B_1\), the linear effect; \(B_2\), the quadratic effect; and \(B_3\), the cubic effect. Following standard method in regression analysis, step-wise deletion of the terms was then applied to remove the non-significant terms, which simplified the model to the final acceptable form. The goodness of fit of the developed equations

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**Table 2:** Composition of the blends in per cent (w/w of blend) is indicated in Table 2. The blend was gelatinized, cast with a thin layer chromatography applicator, dried and the developed film was stored as described elsewhere\(^2,54\). For each composition 10-12 films were cast.
was tested by mean relative percentage deviation modulus (MRE, %) as calculated by the following equation:

\[ \text{MRE} \% = \frac{100}{N} \sum_{i=1}^{N} \frac{|M_{ei} - M_{pi}|}{M_{ei}} \]  

where \( M_{ei} \) is the \( i^{th} \) experimental (mean) value of the response; \( M_{pi} \), the \( i^{th} \) predicted value of the response calculated using the developed equations; and \( N \), the number of experimental data. The value of MRE below 10 % appears to be indicative of a good fit for practical purposes\(^{62}\).

**Optimization using response surface methodology**

Response surface methodology using design expert numerical optimization was applied to optimize the amount of independent variable for getting maximum tensile strength and minimum WVP; equal importance was given for both the properties\(^{63, 64}\).

**Validation of non-linear regression model**

For validation of the developed models, film samples were prepared using the optimized levels of independent variables, and their properties measured. The experimental values of tensile strength and WVP thus obtained were compared with the software displayed predicted values of the polynomial models, and absolute residual error involved in such prediction was calculated\(^{65}\) according to the following equation:

\[ \text{Absolute residual error} \% = \frac{|\text{Experimental value} - \text{Predicted value}|}{\text{Experimental value}} \times 100 \]  

**Statistical analyses**

Treatment effect (Analysis of variance, ANOVA test) of the amount of AM, MC, and HPMC on mean values of tensile strength and WVP of the film was evaluated at 1 or 5% levels of significance using single factor experiment with completely randomized design with equal replications\(^{66}\). Significance of the difference within any two mean values (pair) of the response was tested by evaluating the least significant differences (LSD) at 1 or 5% probability levels\(^{66}\). These calculations were done using Microsoft Excel 2007 (Microsoft Corp., USA).

**Results and Discussion**

Figure 1 represents the mean value along with the standard deviation of tensile strength and WVP of the films containing different levels of AM, MC and HPMC, for binary plasticizer system. Tensile strength in vertical and horizontal direction was comparable, hence the value is average of total 10 replications. For ternary plasticizer system, Fig. 2 similarly represents these properties for AM, MC and HPMC. From the ANOVA it is evident that treatment effect of the levels of FP on tensile strength and WVP, corresponding to both the plasticizer groups, is significant at p<0.01. This rejects the null hypothesis and indicates that film property is controlled by the levels of FP in the blends. Moreover, calculation of
Fig. 2—Effect of concentration of (a) amylose (AM), (b) methylcellulose (MC), and (c) hydroxypropylmethylcellulose (HPMC) on tensile strength and water vapour permeability of films plasticized with glycerol-polyethylene glycol-water

LSD indicates that both tensile strength and WVP of the films change significantly (p<0.01 or 0.05) due to the incorporation of each successive amount of FP.

It is observed from Figs. 1 and 2 that irrespective of plasticizer system, addition of FP increases the tensile strength of film to a maximum value, following a decreasing tendency with further addition. Similar observation is also reported by Turhan and Sahbaz, where films from 3 g MC/100 mL solvent shows tensile strength of 33±3 N/mm², and it drops to 8±1 N/mm² as MC concentration is increased to 6 g MC/100 mL. They concluded that such decrease might be due to partial MC insolubility at higher concentration. Psomiadou et al. mentioned that the improvement in tensile strength with increasing MC content in the starch-MC blend occurs, and according to Peressini et al., it is probably due to the presence of a greater number of interacting molecular chains participating in the formation of the network structure. Improvement in tensile strength by cellulose derivative like HPMC is also observed in films from whey protein isolate–HPMC blend. Formation of denser polymer network due to increase of amylose from 6.3 g to 25.0 g/100 g of starch with concomitant increase in tensile strength from 2.2 MPa to 7.0 MPa has been reported for glycerol plasticized cassava starch films.

For WVP, the reverse trend is observed, i.e. up to a certain limit of FP addition WVP decreases, following an increasing tendency thereafter. Erdohan and Turhan reported that WVP of MC–Gly, and MC-whey protein–Gly films decreases with increasing MC concentration due to the increase in solid content producing small pore size. Le Tien et al. and Coughlan et al. reported that incorporation of polysaccharides into whey protein films decreases WVP. According to de Moura et al., HPMC (3 g/100 mL) film exhibits WVP value of 0.794±0.03 g.mm/kPa.m².h, which is comparable with the present results of starch-HPMC films. Mali et al. prepared films from different sources of starch like cassava, corn, and yam having amylose content of 19, 25, and 29% respectively. They found that films with high amylose content (yam starch) exhibits the lowest WVP at low glycerol content, probably due to the compact structure, and has better characteristics for food packaging films.

The behaviour of corn starch films in the present case may be due to the fact that at lower concentration, the linear chain of FP(s) could form a homogeneous phase with starch improving the tensile strength and WVP; at higher concentration, perhaps, the continuity of the matrix is hampered (phase separation) resulting in poor performance. The concentration, at which such change occurs, is specific to the FP as well as the plasticizer used. Moreover, it is apparent from the figures that the amount at which the maximum tensile strength occurs may not correspond always for minimum WVP, thus necessitating an optimization.
Table 3 — Correlation between each independent variable (functional polysaccharide) with respective film properties

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Regression equations</th>
<th>F-value</th>
<th>Coefficient of determination $r^2</th>
<th>MRE %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary plasticizer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AM</td>
<td>Tensile strength = 12.137+18.018<em>AM-14.791</em>AM</td>
<td>48.290**</td>
<td>0.932</td>
<td>2.764</td>
</tr>
<tr>
<td></td>
<td>WVP = 0.710+0.313<em>AM -0.298</em>AM</td>
<td>729.368**</td>
<td>0.995</td>
<td>0.266</td>
</tr>
<tr>
<td>MC</td>
<td>Tensile strength = 13.578+76.542<em>MC-490.488</em>MC$^2$-5726.619*MC$^3$</td>
<td>58.480**</td>
<td>0.967</td>
<td>2.309</td>
</tr>
<tr>
<td></td>
<td>WVP = 0.685-0.4817* MC -51.245<em>MC$^2$ +456.137</em>MC$^3$</td>
<td>95.730**</td>
<td>0.980</td>
<td>2.952</td>
</tr>
<tr>
<td>HPMC</td>
<td>Tensile strength = 12.202+2.446<em>HPMC +253.548</em>HPMC$^2$ -735.863*HPMC$^3$</td>
<td>138.990**</td>
<td>0.986</td>
<td>1.595</td>
</tr>
<tr>
<td></td>
<td>WVP = 0.722-2.584<em>HPMC +10.205</em>HPMC$^2$</td>
<td>62.080**</td>
<td>0.947</td>
<td>3.650</td>
</tr>
</tbody>
</table>

**Significant at P<0.01. **The non-significant terms of Eq. (2) were deleted by the software computation.

Table 4—Optimum amounts of functional polysaccharides along with their predicted responses and corresponding desirability by software, experimentally determined responses, and absolute residual error involved in validation of the regression models

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Optimum amount of functional polysaccharide %, (w/w of blend)</th>
<th>Predicted responses</th>
<th>Desirability</th>
<th>Experimentally determined responses</th>
<th>Absolute residual error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tensile strength MPa</td>
<td>WVP g.mm/m$^2$.kPa.h</td>
<td>Tensile strength MPa</td>
<td>WVP g.mm/m$^2$.kPa.h</td>
</tr>
<tr>
<td><strong>Binary plasticizer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AM</td>
<td>0.65</td>
<td>17.590</td>
<td>0.629</td>
<td>0.938</td>
<td>17.822±0.010</td>
</tr>
<tr>
<td>MC</td>
<td>0.10</td>
<td>20.326</td>
<td>0.564</td>
<td>0.928</td>
<td>21.001±0.003</td>
</tr>
<tr>
<td>HPMC</td>
<td>0.22</td>
<td>16.694</td>
<td>0.595</td>
<td>0.886</td>
<td>16.894±0.010</td>
</tr>
</tbody>
</table>

| **Ternary plasticizer** |                                                               |                     |                       |                     |                           |
| AM                   | 0.74                                                           | 16.437              | 0.656             | 0.926               | 16.514±0.010             | 0.655±0.008 | 0.466 | 0.154 |
| MC                   | 0.08                                                           | 13.992              | 0.665             | 0.943               | 13.901±0.011             | 0.700±0.060 | 0.655 | 5.000 |
| HPMC                 | 0.29                                                           | 18.200              | 0.852             | 0.836               | 19.580±0.005             | 0.841±0.005 | 7.048 | 1.308 |

Regression analysis

The best fit equations describing the effect of FP on the tensile strength and WVP of the films are reported in Table 3 along with the statistical significance of the equations in terms of F-value (ANOVA), $r^2$, and MRE %. From the F-value it is clear that determination of the effect of AM, MC and HPMC on tensile strength and WVP using the equations are highly significant (p<0.01). The $r^2$ values are also close to 1, and MREs lie within 10%. These suffice the acceptance of the nonlinear models with good fit to the experimental data.

Optimization of level of functional polysaccharide

The optimal amount of FP to be added in the blends for maximizing the tensile strength and minimizing the WVP of the films, for both binary and ternary systems of plasticizers, are reported in Table 4. For binary plasticizer system, these are 0.65, 0.10, and 0.22% respectively for AM, MC, and HPMC and for ternary system, the values are 0.74, 0.08, and 0.29% in that order. Desirability values are high for all the optimum values.

The values of tensile strength and WVP which were determined experimentally for the films containing optimized level of independent variables are also presented in Table 4. Comparing the values with that of the corresponding control (film without FP) as shown in Figs 1 and 2, it is derived that FP(s) in optimized amount could improve the tensile strength of corn starch film by 46 and 23 % (AM), 54 and 2% (MC), and 38 and 46 % (HPMC), for binary and ternary plasticizers respectively.
Similarly, WVP improves by 8 and 26% (AM), 16 and 20% (MC), and 21 and 6% (HPMC) respectively for binary and ternary plasticizer systems.

Validation of nonlinear regression model

In addition to the experimental values of tensile strength and WVP obtained for the films containing optimized level of independent variables, Table 4 also contains the corresponding predicted values as indicated from the software, along with the absolute residual errors calculated using Eq. (4). It is observed that the entire absolute residual error values lie within around 7%, indicating suitability of the model developed, and hence ensuring the optimized level of FP(s) in the blends for maximizing the tensile strength and minimizing the WVP of films.

Conclusion

Response surface methodology using Design Expert numerical optimization could successfully predict the optimum value of amylose, methylcellulose and hydroxypropylmethylcellulose in starch blend to attain maximum tensile strength and minimum water vapor permeability of developed film. For amylose, methylcellulose, and hydroxypropylmethylcellulose, the optimized levels are 0.65, 0.10, and 0.22% in case of glycerol–water plasticizer, and 0.74, 0.08, 0.29% in case of glycerol-polyethylene glycol-water plasticizer respectively.

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