

# Glycerol-plasticized films prepared from starch–poly(vinyl alcohol) mixtures: effect of poly(ethylene-co-acrylic acid)

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Equations were obtained from response surface models to show how the ultimate tensile strength (UTS) and percent elongation at break (%E) of solution-cast films vary with relative amounts of starch, poly(vinyl alcohol) (PVA), poly(ethylene-co-acrylic acid) (EAA) and glycerol in the formulation. Equations found from the response surface methodology were used to optimize the relative amounts of the four components with respect to the physical properties of cast films. The model showed that only glycerol content was important to predict the UTS of the films. The model for %E was more complicated, since there was a three-way interaction between EAA, PVA and glycerol. This model also contained two other terms: a two-way interaction involving glycerol and EAA, and a (PVA)<sup>3</sup> term. In general, %E increased as EAA, PVA and glycerol were increased together. However, increased amounts of EAA could decrease %E if EAA was the only component increased. It is believed that EAA forms complexes with both starch and PVA, thereby increasing compatibility of the two polyhydroxy polymers. As %E increases, UTS of the films decreases. All the films produced in this paper were made with starch contents above 50% to insure an optimum film formulation with at least 50% starch. A mixture of 55.6% starch, 2.8% EAA, 28.3% PVA and 13.3% glycerol is believed to be close to the optimum formulation to obtain films having at least 100%E and UTS of 25 MPa, while still maintaining starch concentrations above 50%.

## INTRODUCTION

Over the last few years, there has been renewed interest in biodegradable plastics and plastics made from annually renewable, natural polymers such as starch. Starch is an abundant water-dispersible, natural polymer that can readily be cast into films (Farrow & Swan, 1923; Neale, 1924). Films have been prepared from a variety of starches (Furry, 1939; Lloyd & Kirst, 1963). Despite their ease of preparation, the physical properties of starch films are poor. Although tensile strengths of the films are high, they are brittle and exhibit little or no elongation (Zobel, 1988; Shogren, 1992; Shogren *et al.*, 1992). In a review of starch as a

biodegradable plastic, Swanson (1992) listed the following target values for physical properties that should be met if starch containing films are to become economically attractive: tensile strength, 4000 psi (27.6 MPa); elongation, 100%; tear strength, 200 g/mil (78N/mm); Mullen burst strength, 15 points; and impact strength, 2 ft-lb/in<sup>2</sup> (4.2KJ/m<sup>2</sup>). Of these values, only tensile strength is regularly met. Because of the poor performance of starch as a plastic, there have been numerous studies devoted to blending synthetic polymers with starch to improve the physical properties of starch films (Doane *et al.*, 1992). Two such synthetic polymers are poly(vinyl alcohol) (PVA) and poly(ethylene-co-acrylic acid) (EAA).

PVA–starch films containing 51% starch, 17% PVA, 30% plasticizer, 1% paraformaldehyde and 1% NH<sub>4</sub>Cl were investigated by Westhoff *et al.* (1979). They observed that film properties varied with the type of

\* The mention of firm names or trade products does not imply that they are endorsed or recommended by the US Department of Agriculture over other firms or similar products not mentioned.

plasticizer used. Although good physical properties were obtained initially, they deteriorated over time. Mixtures of PVA and starch are, however, used commercially to produce water-soluble laundry bags (Otey & Doane, 1984), and a derivatized starch is used in the formulation to enhance the bag's solubility.

EAA-starch films have been prepared by Otey *et al.* (1974, 1980, 1987) for application as biodegradable mulch and packaging. Solution cast EAA-starch films containing more than 40% starch deteriorated within 7 days when exposed to soil microorganisms (Otey *et al.*, 1977). However, films containing 30–40% starch remained flexible and provided mulch protection for up to 70 days. Further work on EAA-starch films (Otey *et al.*, 1980; Otey & Westhoff, 1982) showed that starch-EAA mixtures containing up to 60% starch could be processed into films by extrusion blowing. Films containing 60% starch had poor physical properties when compared with Swanson's (1992) list of optimal physical properties, although reducing the starch content to 40% yielded good quality films.

Mixing an aqueous ammonia solution/dispersion of EAA with an aqueous solution of starch results in a pronounced increase in solution viscosity (Maxwell, 1970; Fanta & Christianson, 1991; Christianson *et al.*, 1992; Fanta *et al.*, 1992). A helical inclusion complex between starch and EAA (Fanta *et al.*, 1990; Fanta & Salch, 1991; Shogren *et al.*, 1991*a,b*), analogous to the well-known fatty acid starch complex, was proposed to account for this viscosity increase. Addition of EAA increases the viscosity of starch solutions by complexing with more than one starch molecule and thereby increases the effective molecular weight of starch through formation of pseudo cross-links (Fanta & Christianson, 1991; Christianson *et al.*, 1992; Fanta *et al.*, 1992). PVA also forms helical inclusion complexes (Zwick, 1965) with iodine, analogous to those formed in starch. Although Maxwell (1971) reported outward compatibility of PVA and EAA, he did not observe the large viscosity increases he had encountered with the starch-EAA system.

Since EAA not only forms a helical inclusion complex with starch but also has the potential for complexing with PVA, starch and PVA could conceivably become bound together through simultaneous complex formation with a single EAA molecule. Formation of such a starch-EAA-PVA complex, even in minor amounts, might enhance the compatibility of starch and PVA significantly and thus improve film properties. This study was therefore carried out to determine the effect of EAA addition on the physical properties of starch-PVA films. Although many polyols have been reported as plasticizers for starch-containing films, we have used glycerol for this initial study. Our intent in this study was to come up with a model that would allow us to maximize the amount of starch in the formulation.

## MATERIALS AND METHODS

### Materials

Unmodified commercial grade cornstarch (Buffalo 3401) was obtained from CPC International Inc. (Argo, Illinois). PVA was obtained from Air Products and Chemicals, Inc. (Allentown, Pennsylvania) under the trade name Airvol 325. Airvol 325 was 98–98.8% hydrolyzed with a molecular weight average of 85 000–146 000. EAA was obtained from Dow Chemical Co. (Midland, Michigan) under the trade name Primacor 5981. This EAA had an  $M_w$  of about 18 000 and an  $M_n$  of about 7000, and contained about 20% acrylic acid. Reagent grade glycerol was from Fisher Scientific.

A 10% (w/w) solution/dispersion of EAA in aqueous ammonium hydroxide was prepared as described by Fanta *et al.* (1992). A 10% (w/v) solution of PVA was prepared by adding 800 g of solid PVA to 6500 ml of water. The mixture was slowly heated under constant stirring until it reached 95°C and then heated for an additional hour. When the solution had cooled, water was added to bring the volume to 8000 ml.

### Mixing of ingredients

The liquid ingredients, i.e. EAA, glycerol and PVA, were weighed out into flasks. Enough water was added to the ingredients to make a final solids content after jet cooking of around 10%. The liquids were then mixed with the pre-weighed starch in large beakers. The starch was mixed thoroughly with the liquid to give a dispersion and mixed periodically to keep the starch from settling to the bottom.

### Jet cooking

Jet cooking (Winfry & Black, 1964) was carried out using a Penick and Ford (Penick and Ford Ltd, Cedar Rapids, Iowa) laboratory model continuous cooker. The method involves pumping a starch-containing dispersion through an orifice where it contacts a jet of high pressure steam. Cooking took place with 70 psig (4.9 Kg/cm<sup>2</sup> line pressure steam and was carried out at 140°C (40 psig steam) (2.8 Kg/cm<sup>2</sup>) with a pumping rate of about 1.1 liter/min. Under these high-temperature, high-shear conditions, starch granules are totally disrupted. The final solution contains little or no insoluble starch. The cooked solutions were collected in dewar flasks to maintain their temperature at approximately 90°C until the films were cast. All components of the formulation were mixed before jet cooking. The solids content of the initial mixture before jet cooking was adjusted so that the jet cooked solution would have a solids content of about 10%.

## Film preparation

The jet-cooked solutions were cast at 50-mil (1.25mm) wet thickness onto preheated glass plates (95°C). To prevent the film from sticking to the glass plate, a release paper (S.D. Warren Co. South Portland, Maine) was glued to the plate with a silicon adhesive. After the films had been cast, they were placed in a humidity cabinet and dried overnight at 50°C and 50% relative humidity. After drying, the films were kept at 25°C and 50% relative humidity for 7 and 28 days before testing.

## Mechanical testing

UTS and %E were evaluated for each film using an Instron universal testing machine. Four dog-bone shaped specimens (ATSM D412-68, Type C) were cut from each film. Specimens had a width of 6.35 mm. Each piece was measured for thickness in three places along the test length using a Mini Test 3000 (Elektro-Physik, Cologne, Germany). The specimens' averaged thickness was about 0.1 mm. The gauge length and grip distance were both 50.8 mm. Crosshead speed of the Instron was 50 mm/min, with a data collection rate of 20 pts/s. Tests were carried out at 25°C and 50% relative humidity. Averages of the four values obtained for UTS and %E were used for the response surface analysis outlined below.

## Experimental design

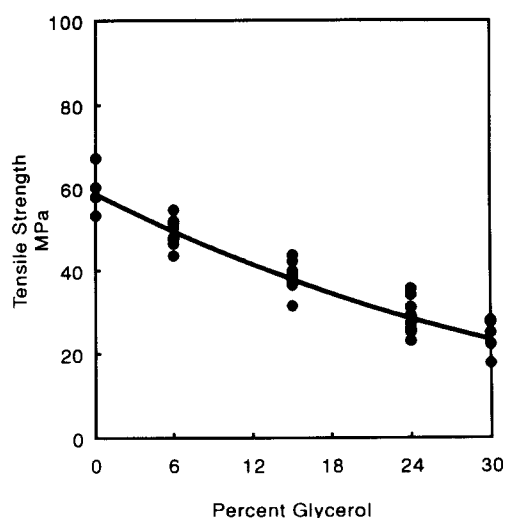
Five treatment levels, based on starch, of EAA (0, 1.2, 3, 4.8 and 6%), PVA (20, 28, 40, 52 and 60%) and glycerol (0, 6.15, 24 and 30%) were studied. Fifteen of the possible 125 combinations were selected for testing according to a central composite rotational design (Cochran & Cox, 1957). Six replicates of the center point of the design were also tested, giving a total of 20 tested films. Thirty-one additional films were added to the model to obtain a more thorough response surface at the corners. Film data was analyzed by the regression analysis portion of the SAS program (SAS Institute Inc., Raleigh, North Carolina, 1992 release).

## RESULTS AND DISCUSSION

A stepwise SAS procedure was used to find a regression model for the dependent variables, UTS and %E. The model found for UTS was

$$\text{UTS} = 58.61 - 1.596(\text{GLY}) + 0.014(\text{GLY})^2 \quad (1)$$

where GLY is percent glycerol in the film based on starch. Figure 1 shows the graphical form of the equation along with the experimental data. UTS of the films decreased as glycerol content of the films increased; this



**Fig. 1.** Tensile strength of the cast film as a function of glycerol content. Equation of the fitted line is  $\text{UTS} = 58.61 - 1.596(\text{GLY}) + 0.014(\text{GLY})^2$ , with an  $R^2 = 0.89$ .

is a well-documented phenomenon for plasticizers in synthetic polymers (Sears & Touchette, 1989). The regression equation has an  $R^2$  of 0.89 that is highly significant. Attempts to add the other independent variables (EAA and PVA) to the model, either independently or as interactive cross products, were always rejected statistically. UTS is thus influenced only by the glycerol content of the cast films and not by the amount of EAA and PVA present.

The fact that the EAA content of the film did not effect UTS was surprising since our original premise was that EAA was complexing with both starch and PVA. If a complex is formed between starch, PVA and EAA, the UTS would be expected to increase with increases in EAA at a given glycerol content. Figure 1 does show some scatter around points where the glycerol content is held constant. However, the scatter could not be explained by the EAA content of the films. One reason for this may be that the PVA content of these films was also not held constant. Consequently, both the PVA and EAA were varied at these points. Thus, if the effect of EAA on UTS is small compared with the effect of glycerol, the EAA effect could be lost in the error associated with the test. The influence of glycerol and EAA content of the films on UTS is currently being studied.

The model found for %E of the films was also obtained by the SAS procedure. The best model found for %E was

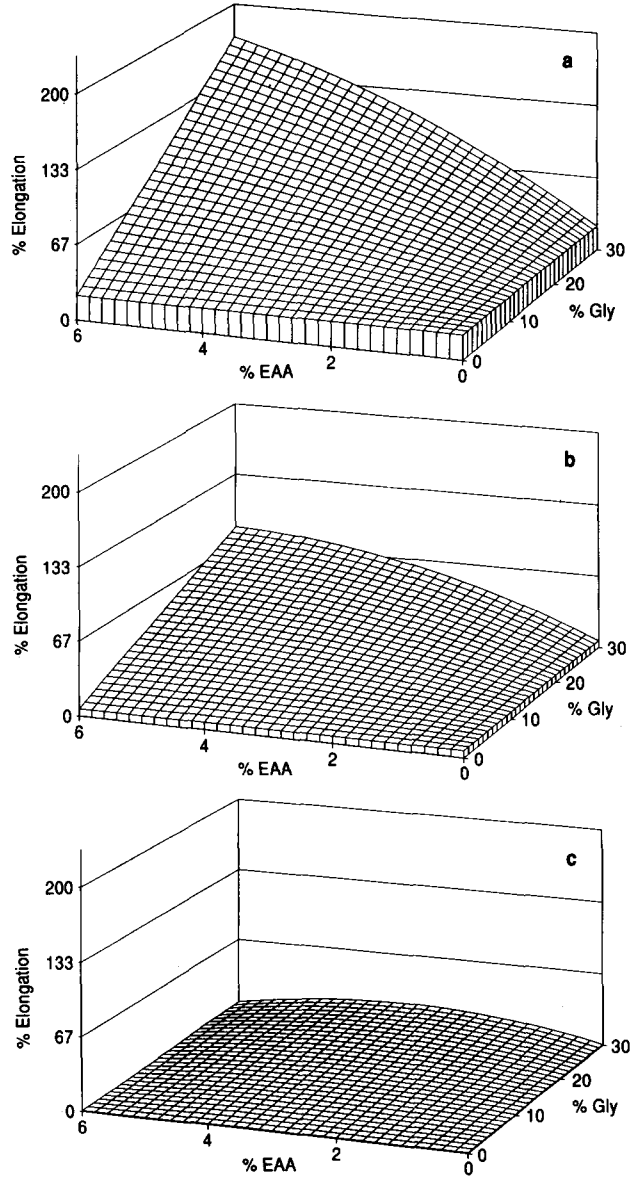
$$\begin{aligned} \%E = & 0.0197(\text{EAA})(\text{PVA})(\text{GLY}) - 0.06003 \\ & (\text{EAA})^2(\text{GLY}) + 0.0001(\text{PVA})^3. \end{aligned} \quad (2)$$

The term for the intercept was not significantly different from zero and was therefore left out of the model. Response surface plots obtained from the predicted equation are shown in Figs 2–4. In general, the surface

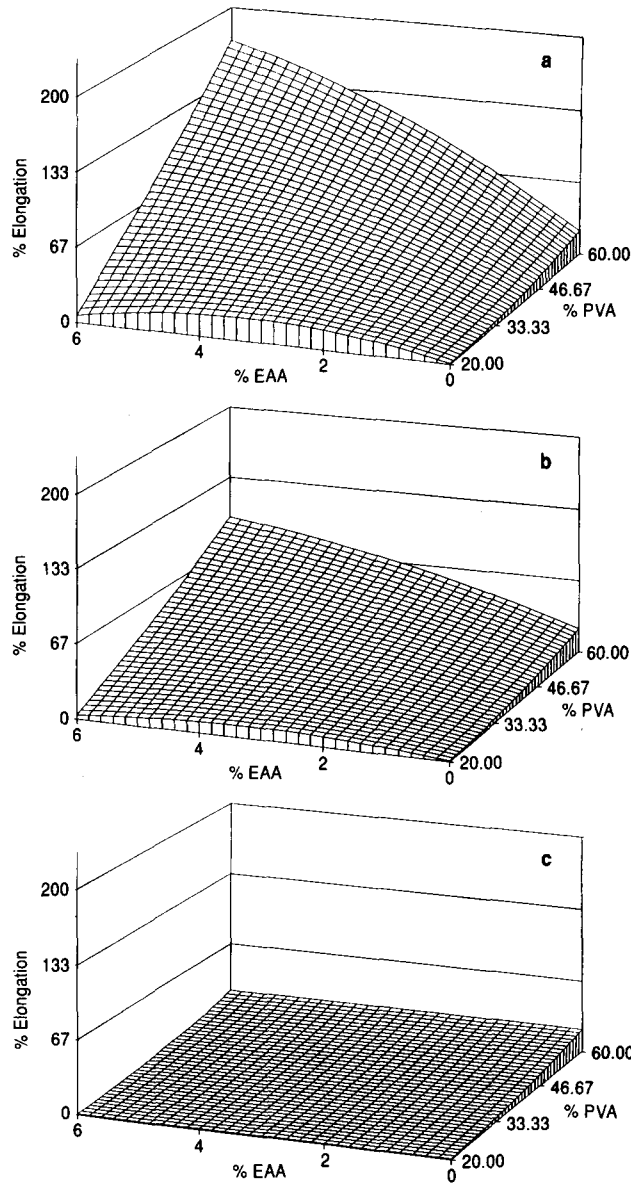
plots of the model show that %E increases as EAA, PVA and glycerol concentration increases. The exception to this is when the EAA content of the film is high and the PVA content is low. The predicted model shows a significant three-way interaction between the independent variables EAA, PVA and glycerol. This interaction explains about 85% of the variation in the data. Part of this interaction is related to the starch content of the film, since starch content decreases in the film as the concentrations of EAA, PVA and glycerol increase in the film. A film with less starch and more synthetic polymer would be expected to have a greater %E. However, this does not explain all of the EAA\*PVA\*GLY interaction. When a regression model

was obtained for percent starch in the film versus %E, only 36% of the variation could be explained by percent starch in the film. However, 85% of the variation in the data could be explained by a regression model with the EAA\*PVA\*GLY interaction term.

The EAA\*PVA\*GLY term can explain about 49% more of the variation in the data than can percent starch. This greater ability of the EAA\*PVA\*GLY term to explain the data can be seen by examining the data more closely. A film made with 52.6% starch (60% PVA and 30% glycerol based on starch) had a %E of about 27, whereas a film containing a greater percentage of starch, 55.6% starch (51% PVA, 24% glycerol, and 5% EAA base on starch) had a %E of 105.2, almost four times greater. The difference between these is that the latter film contains a small amount of EAA (only



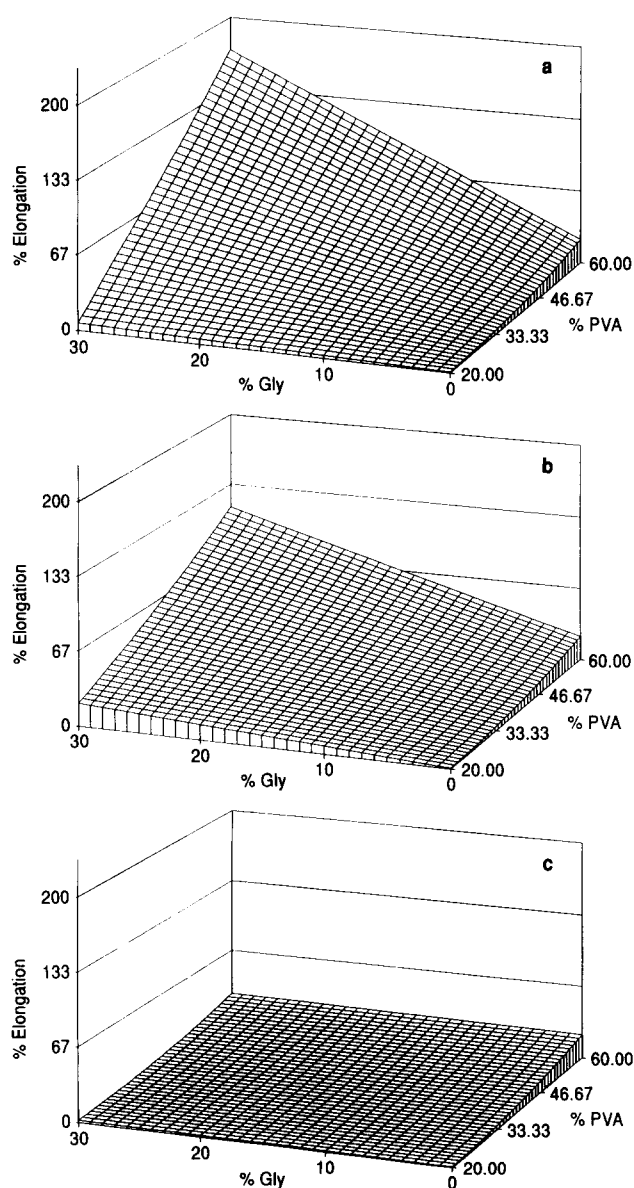
**Fig. 2.** Response surface plot of %E against percent EAA and percent glycerol. The surface equation is (eqn (2))  $\%E = 0.0197(EAA)(PVA)(GLY) - 0.06003(EAA)^2(GLY) + 0.0001(PVA)^3$ . a, PVA = 60%; b, PVA = 40%; c, PVA = 20%.



**Fig. 3.** Response surface plot of %E against percent EAA and percent PVA. The surface equation is the same as in Fig. 2. a, glycerol = 30%; b, glycerol = 15%; c, glycerol = 0.1%.

2.8% EAA of the whole film concentration), implying some kind of interaction involving EAA. A possible explanation for this interaction is our original premise that EAA complexes with both the starch and PVA, thereby helping to make these two polyhydroxy polymers compatible.

The interaction of EAA and the other components is also seen in the films themselves. When PVA and Glycerol are in the films at high concentrations, the concentration of EAA is critical. If EAA is not added at high enough concentrations, the starch and PVA components of the film phase separate during the drying step. This was seen very clearly by the splotchy films that are produced. The phase separation does not occur if the EAA concentration is increased or the PVA concentration decreased.



**Fig. 4.** Response surface plot of %E against percent PVA and percent glycerol. The surface equation is the same as in Fig. 2. a, EAA = 6%; b, EAA = 3%; c, EAA = 0.1%.

The interaction term EAA\*GLY is negatively related with %E. This can be seen in Fig. 2(c) and in Fig. 4(a), where the PVA content in the film is low. A possible reason for the negative influence of the EAA\*GLY term to elongation could be that glycerol acts as a so-called antiplasticizer for the starch-EAA system. Also EAA in films with low amounts of PVA could complex with starch to such an extent that it makes the resulting film less extensible by overly cross-linking the starch to itself.

The PVA term in the model has a positive effect on elongation, as expected because of the good elongation observed in films prepared from pure PVA (Toyoshima, 1975). Indeed it was the good physical properties of PVA along with its water compatibility that led us to mix it with starch to upgrade starch properties.

Films equilibrated for 28 days rather than 7 days at 50% RH generally showed a decrease in elongation and an increase in tensile strength, in agreement with other studies with starch-containing films (Westhoff *et al.*, 1979; Otey *et al.*, 1987; Shogren 1992; Shogren *et al.*, 1992). It is noteworthy that films with 0% glycerol actually decrease in UTS after 28 days, rather than increase like the other films. It is possible that 7 days at 50% RH was not long enough to equilibrate this film, whereas after 28 days the films had enough time to absorb sufficient moisture to lower their initial tensile strengths. Equilibration of film samples at relative humidities lower than 50% severely reduced %E and increased UTS, indicating the importance of the plasticizing effect of water.

The overall goal of this study was to find a combination of starch, EAA, PVA and glycerol which contained at least 50% starch and produced films having a %E of at least 100 and a UTS of above 25 MPa. The surface response graphs (Figs 2-4) along with Fig. 1 show that a formulation close to optimum would be about 55.6% starch, 2.8% EAA (5% based on starch), 28.3% PVA (51% based on starch) and 13.3% glycerol (24% based on starch).

## CONCLUSIONS

The addition of small amounts of EAA to cast films containing starch, PVA and glycerol can improve the elongation of the film significantly over films containing no EAA. A statistical model was built to predict the response of %E as the amounts of EAA, PVA, and glycerol varied and showed that %E depended positively on an EAA\*PVA\*GLY interaction, negatively on a GLY\*EAA interaction, and positively on PVA. EAA is thought to form helical inclusion complexes with both starch and PVA, thus making the two polyhydroxy polymers compatible. Too much EAA in the film complexes the starch to the extent of making the film brittle, whereas too little EAA could lead to a phase separation between PVA and starch. A statistical model

was also built for UTS, but only the glycerol content of the film was shown to be significant. A film containing 2.8% EAA, 28.3% PVA, 13.3% glycerol and 55.6% starch was chosen as the best combination of ingredients to obtain a film with acceptable values for both %E and UTS. In future work, films made with this combination of starch, EAA and PVA will be made with plasticizers other than glycerol in an attempt to improve film properties. Additional work is underway to understand further the nature of the interaction between EAA, PVA, plasticizer and starch.

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