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# Effect of different plasticizers on mechanical, thermal, and barrier properties of corn starch/polyvinyl alcohol/rice husk flour based bio-composite films

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The current research is intended to correlate the impact of glycerol, sorbitol, fructose as a plasticizer with different concentration (10, 20, 30, and 40%) on the properties of biodegradable corn-starch (CS)/polyvinyl alcohol (PVA)/rice husk flour (RHF) based films. The film was prepared by solvent casting techniques and investigated for the structural, thermal, barrier and mechanical, properties of the produced films. The results indicated that the fructose based plasticized films displayed remarkable tensile strength than glycerol and sorbitol-based plasticized films. Regardless of plasticizer types, increment in plasticizer content enhances water vapor permeability from $5.755\times10^{-10}$ to $9.760\times10^{-10}$ $g\cdot m^{-1}\cdot s^{-1}\cdot Pa^{-1}$. Thermal resistance of the glycerol plasticized film was lower when contrasted with the sorbitol and fructose based plasticized film. The 10% fructose plasticized film indicated great attributes and provided the most extreme mechanical performance among the plasticizers utilized.

Keywords: Corn-starch, polyvinyl alcohol, rice husk flour, mechanical properties, bio-composite films, barrier properties, structural properties, plasticizers.

## Introduction

A large portion of the packaging materials used today is produced using petroleum-based synthetic polymers. These synthetic materials can't be easily disposed of. Right now, making of edible films assumes a huge job in food preservation. Based on biodegradability, accessibility, sustainability, non-poisonous quality, and affordability, starch is one of the most reassuring of all the biopolymer materials[1,4]. About, 85% of world starch is extracted from the corn tree. In spite of the numerous focal points of starch, it has inherent disadvantages, such as poor mechanical properties and high water sensitivity[5,8]. In this context, it is important to incorporate reinforcing materials, for example, plasticizers in pure starch to improve its feasibility and to suppress the fragility of the film[9,10]. The principle function of the plasticizers is to improve the elasticity and functionality of the starch. This examination, proposes to assess the impact of plasticizers namely, glycerol, sorbitol, fructose with concentrations (10, 20, 30 and 40%) on mechanical, thermal, structural and barrier properties of corn-starch/polyvinyl alcohol/rice husk flour bio-composite films.

## Experimental

*Materials:*

The corn starch used in this investigation was procured from the nearby market, Pune, Maharashtra. Polyvinyl alcohol (PVA-M.W. 20,000) was bought from Acrylamide India. Glycerol, sorbitol, fructose were purchased from Estelle Chemicals, Maharashtra, India. Rice husk was acquired from a local rice factory (Maharashtra, India) for reinforcement in starch/PVA bio-composites.

*Methods:*

*Film preparation and characterization:*

The biodegradable film based on corn-starch (CS)/polyvinyl alcohol (PVA)/rice husk flour (RHF) was prepared by casting process. Glycerol (G), sorbitol (S) and fructose (F) have been used as plasticizers. The film preparation tech-

niques are delineated as follows: Initially, 2 g of corn-starch was dissolved in 100 ml of distilled water and heated with a steady magnetic stirrer at 75°C for 10 min. At that point, 1 g of PVA and 1.5 g of rice husk flour were added to the starch and afterward again mixed at 95°C for 10 min. Subsequently, 0.5 g of the plasticizers (G, S, F) were also incorporated into the dispersions. Additional 15 min stirring of the mixture was carried out at 95°C and solutions was allowed to cool on a circular plate (10 cm diameter) for film forming. At 50°C temperatures the new casted films were dried in an oven. After drying prepared films were detached from the plates and put away at ambient conditions (around 25°C and 60% of relative humidity).

*Tensile properties:*

For the films measurement of elongation at break (EB) and tensile strength (TS) were done using standard ASTM D882 method. The crosshead speed was adjusted to 2 mm/min with a 30 kg load cell. The films were cut like strip with size 10 mm×70 mm. The sample has 0.10 mm average thickness. Between the grips the strips of 10 mm×70 mm were placed and the initial gauge length was adjusted to 30 mm. Measurements were made on 5 different specimens.

*Water vapor permeability (WVP):*

Standard ASTM E96-95 method was used to perform the water vapor permeability test (WVP). According to the method, the film samples were placed on a tube shaped cup containing 20 g of silica gel. Then, both the weight gained by the test cup and the weight of the test cup were measured. The WVP was calculated by the formula;

$$\text{WVP} = \frac{n \times d}{A \times T \times P} \quad (1)$$

where, area of the film is $A$ ($m^2$), $n$ (g) is the obtained weight of the test cup; $d$ (mm) is thickness of the film; the partial pressure of water through the films is $P$ (Pa), and $T$ (s) is time period for permeation.

*Thermal properties:*

*Differential Scanning Calorimerty (DSC):*

According to the test procedures, in an aluminum sample pan, the 10 $mm^2$ film sample was placed with an empty aluminum pan reference. The sample was allowed to heat ranging between 25°C to 260°C with constant heating rate 10°C/min. The peak temperature ($T_p$) and onset temperature ($T_o$) were noted.

## Results and discussion

*Mechanical properties:*

The elongation at break (mm) and tensile strength (MPa) were determined from the tensile test. The effects of various plasticizers (F, S, G) (with varying concentrations (10%, 20%, 30%, 40%)) on the mechanical properties (elongation at break; EB and tensile strength; TS) of CS/PVA/RHF films are shown in the Fig. 1 and Fig. 2.10% fructose plasticized film shows highest elevation in tensile strength (25.9 MPa), which is higher than the reported value of 14.9 MPa for CS/PVA/RF film plasticized with 10% glycerol and 10.21 MPa for CS/PVA/RHF film plasticized with 10% sorbitol. Films containing 40% glycerol indicated the lowest tensile strength values, due to their hygroscopic nature which provided extra water in the film matrix[11]. The tensile strength of the fructose plasticized films has been significantly lessen from 25.92 to 23.81 MPa, for the films plasticized with sorbitol; reduced from 14.91 to 12.66 MPa, for the films plasticized with glycerol from 10.21 to 8.22 MPa as plasticizer concentration expanded from 10% to 40%[12,13]. As envisioned, the increase in the concentration of plasticizer from 10 to 40% enlisted an extensive increment in the elongation of film: 25.22– 38.44% for G-plasticized films, 24.44–28.22% for S-plasticized films and 23.23–29.44% for F-plasticized films. The observed increment in the elongation of film is due to the fact that the plasticizers causes reduction of intermolecular forces which exists in between amylose and amylopectin molecules and replace them with hydrogen bonds. It causes the flexibility and reduction of the tensile strength.

*Thermal properties:*

DSC is a general method to determine thermal properties of film such as $T_p$; peak temperature and $T_o$; onset temperature. If the values of $T_p$ and $T_o$ are very close during sealing, melting of film would occur. Table 1 manifest the consequence of addition of various plasticizers on $T_o$ and $T_p$ of the CS/PVA/RHF films. The $T_o$ and $T_p$ of the controlled

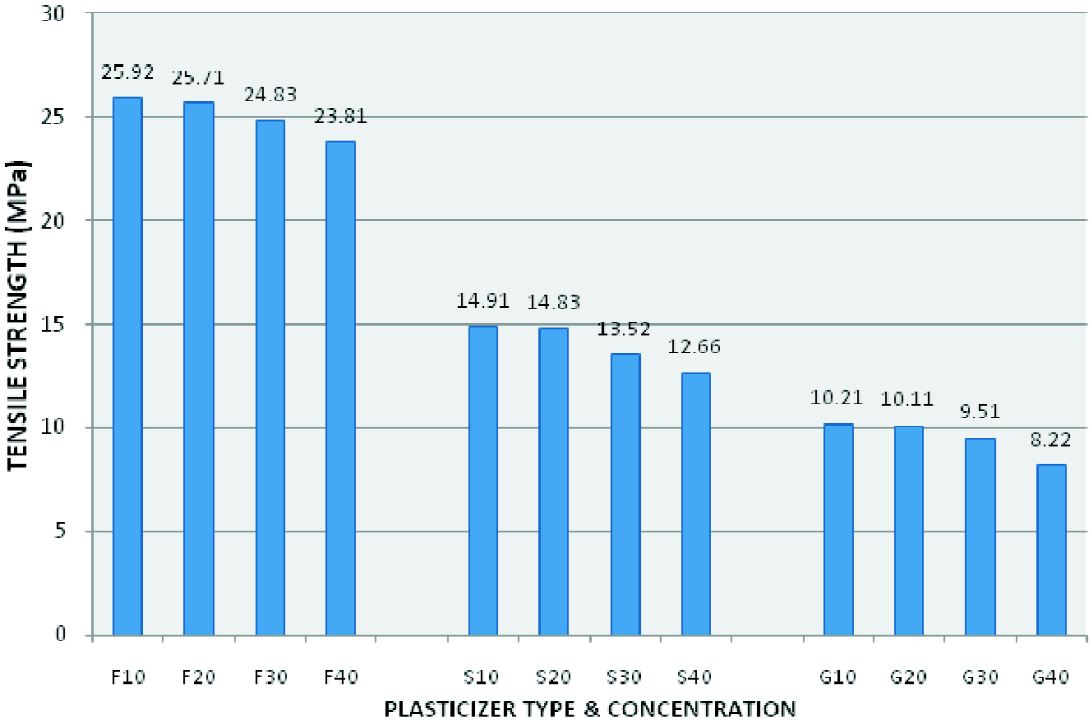


**Fig. 1.** Effect on tensile strength of CS/PVA/RHF films with varying concentration and type of plasticizer.

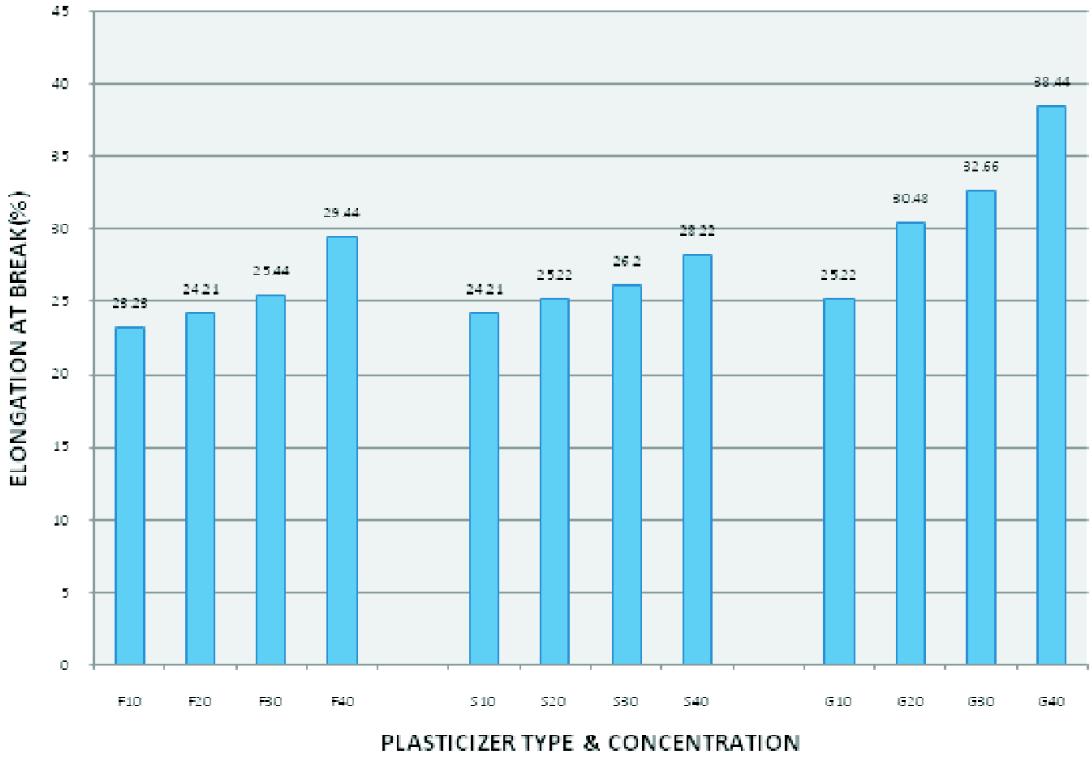


**Fig. 2.** Effect on elongation at break of CS/PVA/RHF films with varying concentration and type of plasticizer.

films are 135°C and 147.5°C, respectively. The addition of plasticizers diminishes all films $T_o$ and $T_p$. In the case of F-plasticized film, when the concentration of plasticizer increased from 10 to 40% $T_o$ diminished from 160°C to 150.2°C and the $T_p$ diminished from 190.6°C to 180.3°C. On account of S-plasticized film, $T_o$ diminish from 150°C to 140°C and $T_p$ diminished from 180°C to 170.1°C with increase the concentration of sorbitol from 10 to 40%. For G-plasticized film lowest $T_o$ and $T_p$ was observed. $T_o$ and $T_p$ diminished from 140°C to 136°C and from 160.2°C to 149.8°C, respectively because of the creation of strong hydrogen bonds between the starch and plasticizers[14].

**Table 1.** DSC results of CS/PVA/RHF film with varying concentration and type of plasticizer

| Film sample | $T_o$ (°C) | $T_p$ (°C) |
|---|---|---|
| Control film | 135 | 147.5 |
| F10 | 160 | 190.6 |
| F20 | 158.2 | 189.5 |
| F30 | 157.3 | 185.4 |
| F40 | 150.2 | 180.3 |
| S10 | 150 | 180.6 |
| S20 | 148 | 176.2 |
| S30 | 145 | 174.2 |
| S40 | 140 | 170.1 |
| G10 | 140 | 160.2 |
| G20 | 138 | 151.1 |
| G30 | 137 | 151.0 |
| G40 | 136 | 149.8 |

*Water Vapor Permeability (WVP):*

It is an indispensable attribute for the packaging of vital foods. So, the WVP ought to be as low as possible of the food packaging material. The impact of types and concentration of plasticizer on the WVP of the CS/PVA/RHF film is shown in Table 2. As appeared in Table 2, the WVP estimations of plasticized CS/PVA/RHF films is increased with the concentration of the plasticizer (10–40% w/w). According to data displayed in Table 2, results of water vapour permeability raised from $7.445\times10^{-10}$ to $9.760\times10^{-10}$ g·s$^{-1}$·m$^{-1}$·Pa$^{-1}$, $5.755\times10^{-10}$ to $7.545\times10^{-10}$ g·s$^{-1}$·m$^{-1}$·Pa$^{-1}$ and $6.845\times10^{-10}$ to $8.444\times10^{-10}$ g·s$^{-1}$·m$^{-1}$·Pa$^{-1}$ for G-plasticized, F-plasticized and S-plasticized films, respectively. WVP values of film increases regardless of the types of plasticizer. 10% fructose plasticized CS/PVA/RHF film demonstrated much lower WVP. As it may be a result of well built link between the starch-starch molecules, resulted denser and more compact starch structure and network. It is also observed that G-plasticized films own higher WVP values in contrast to plasticized films of S and F. This may be attributed to the intrinsic hydrophilic nature of glycerol which promotes a commendable absorption of water molecules. This fact also supports high value of WVP for the starch-based films unlike the synthetic plastic films.

**Table 2.** Effect on water vapour permeability (WVP) of CS/PVA/RHF films with varying concentration and type of plasticizer

| Film sample | Type of plasticizer | Plasticizer concentration (%) | WVP×10$^{-10}$ (g·s$^{-1}$·m$^{-1}$·Pa$^{-1}$) |
|---|---|---|---|
| F10 | Fructose | 10 | 5.755±0.02 |
| F20 | Fructose | 20 | 6.742±0.04 |
| F30 | Fructose | 30 | 6.889±0.05 |
| F40 | Fructose | 40 | 7.545±0.06 |
| S10 | Sorbitol | 10 | 6.845±0.02 |
| S20 | Sorbitol | 20 | 6.899±0.01 |
| S30 | Sorbitol | 30 | 7.454±0.04 |
| S40 | Sorbitol | 40 | 8.444±0.05 |
| G10 | Glycerol | 10 | 7.445±0.06 |
| G20 | Glycerol | 20 | 7.898±0.04 |
| G30 | Glycerol | 30 | 8.992±0.06 |
| G40 | Glycerol | 40 | 9.760±0.01 |

## Conclusions

The impacts of various plasticizers used in the synthesis of CS/PVA/RHF based film were significant especially on the water vapour permeability, mechanical, and thermal properties of the synthesized films. The addition of plasticizer enhances the water vapour permeability and elongation at break and at the same time it reduces the tensile strength and thermal properties. Overall, the present investigation has confirmed that variations in the type and concentration of plasticizers influence the barrier, mechanical and thermal properties of synthetic CS/PVA/RHF films.

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