

A Study on Biodegradable Water Soluble Film Based on Blend of Polyvinyl Alcohol and Modified Thermoplastic Cassava Starch

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Abstract: In this study, we present a novel approach to enhance the mechanical properties of Polyvinyl alcohol/modified thermoplastic cassava starch (PVA/MTPS) films through the integration of citric acid (CA) and plasticizer using blown film extrusion. By employing the CA-PVA-MTPS cross esterification mechanism and the multi-carboxyl functionalities of CA, we achieved substantial improvements in intermolecular interactions. This resulted in the formation of robust hydrogen bonds, leading to enhanced cross-linking and hydrogen bonding within the film matrix. Notably, the optimized film composition, comprising 30wt% plasticizer content and 4wt% CA, demonstrated exceptional tensile strength, reaching 11.2 MPa (at 55-65% RH) and 9.8 MPa (at 80-85% RH). Our findings highlight the successful utilization of CA as an innovative additive strategy for enhancing the mechanical performance of PVA/MTPS films.

Keywords: PVA, biodegradable, citric acid, modified thermoplastic starch, water soluble film

I. INTRODUCTION

The use of petroleum-based plastic products has been continuously increasing due to low cost, ease of processing and high durability. Unfortunately, such an increase in plastic consumption results in an immense amount of non-degradable waste and pollution. To tackle this problem, many efforts have been made to develop environmentally friendly materials [1]. PVA and starch are both biodegradable and exhibit hydrophilic properties, which promotes their compatibility with each other. Moreover, the inclusion of PVA in starch enhances both the thermal and mechanical properties of the material, resulting in modifications to the polymer structure at both the molecular and morphological levels [2-5]. However, the mechanical and physical properties of PVA/starch blended systems are generally inferior to those of conventional polymers [6].

Citric acid (CA), which is the primary organic acid found in citrus fruits and pineapples, is a candidate to enhance the mechanical properties of PVA/starch blends. It presents in abundance with one hydroxyl group and three carboxyl groups [7]. The addition of citric acid to hydroxyl-bearing polymer chains under gentle conditions offers a straightforward method to significantly enhance their mechanical properties and water stability [8]. Furthermore, by employing citric acid as a crosslinking agent, the need for high temperature processing can be circumvented, thus preventing potential harm to starch molecules. The primary mode of crosslinking involves the hydroxyl groups found in both PVA and starch, leading to an enhancement in the interaction of polymer chains through improved hydrogen bonding [9].

Besides the effect of additive component to mechanical and barrier properties of PVA/starch blends, fabrication method also affects these properties. PVA/starch film have also fabricated using methods such as solution casting, extrusion, or compression molding, but these methods are not suitable for large-scale production due to high processing costs and low efficiency compared to extrusion blowing [1]. Among them, blown film extrusion has been known for the ability to produce thinner and more durable films, compatibility with a wide range of materials, efficient utilization of resources, and the capability to manufacture products such as bags and packaging materials [10]. Therefore, PVA/starch films produced by the extrusion blowing should be further studied, not only for reducing production cost, but also for obtaining the desired properties of the end products used in practical applications.

In this study, a biodegradable PVA/MTPS (modified thermoplastic starch) blend films were prepared by using two-step compounding and subsequent blown film extrusion. The presence of citric acid in MTPS improved the microstructures melting index of the blend, the mechanical properties our films. With excellent mechanical and physical characteristics, our material is a potential candidate for the ultimate goal of replacing non-ecofriendly materials by biodegradable materials in various applications.

II. MATERIAL AND METHODS

2.1. Materials

In this paper, we used hydroxypropyl distarch phosphate (the hydroxypropyl group content is 4.4g/100g starch) which is the modified Vietnamese cassava starch. PVA (Kuraray, Japan) was of alcoholysis degree of

88%. Glycerol (Malaysia). Polyethylene glycol (PEG), CA (China) were industrial grade and were used as received. Calcium carbonate (CaCO₃) powder with particles size about 10 μm was from Vietnam.

2.2. Preparation of the PVA/MTPS film

The fabrication of PVA/MTPS (modified thermoplastic starch) film was carried out according to the scheme illustrated in Figure 1.

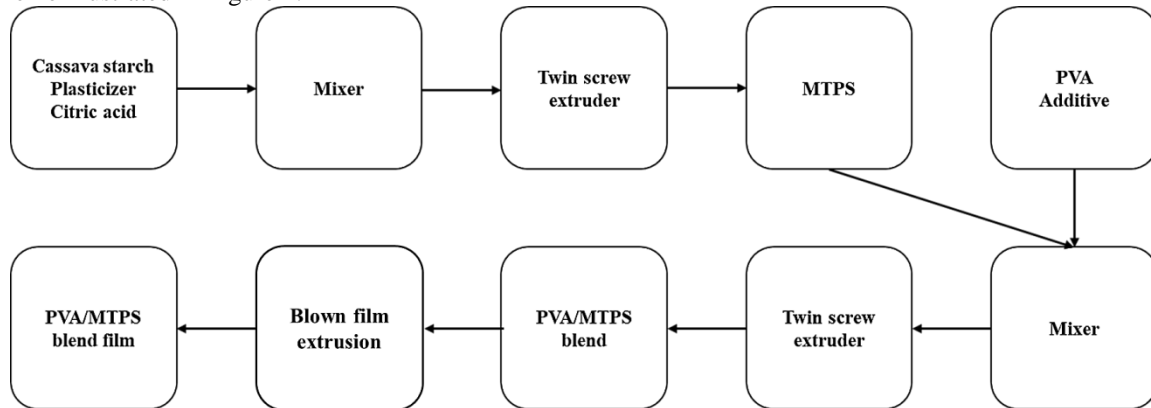


Fig. 1 Preparation scheme of PVA/MTPS blend film

Firstly, starch, plasticizers (including glycerol, PEG4000 at ratio 80:20) and CA were mixed for 15 minutes at room temperature. The mixtures were packaged in polyethylene bags and stored for at least 24 hours at room temperature to allow all the components to reach equilibrium. The mixture was then fed into a twin-screw extruder operating at a screw speed of 150 rpm. The temperature zones were respectively 120, 140, 160, 170, 170, 170, 170, 160, 150, and 140 °C. The MTPS product obtained after mixing was cooled and cut into pellets, dried for 3-4 hours at 85 °C.

Next, PVA, MTPS (at weight ratios of PVA/MTPS is 60/40), and the additive were pre-mix in a mixer and fed into a twin-screw extruder of which the temperature zones were respectively 100, 150, 190, 190, 190, 190, 190, 190, and 180°C. The screw speed was 250rpm. The extruded blends were cooled and cut into pellets and dried for 3-4 hours at 85°C.

Finally, the film samples were prepared using the Labtech blown film extrusion with a screw speed of 40rpm and barrels temperatures from feed zone to the die zone at 180, 190, 190, 195, 195, 190, and 190°C.

2.3. Characterization methods

2.3.1. Mechanical characterization

The tensile strength and elongation at break tests were performed according to ISO 527 using LLOYD 5kN machine with crosshead speed of 300mm/min. Before analyzing, the samples were stabilized for 24 hours at the temperature of 25°C, with a humidity of 55-65%. Each sample was repeatedly tested for 10 times. The results were then averaged.

Additionally, the effects of humidity on the tensile properties of PVA/MTPS blends were also studied. To control the humidity, samples were stored for 72 hours in a sealed vessel with 80-85% humidity (80-85% humidity is KCl salt saturated environment).

The tensile strength values were calculated using the following formula:

$$\sigma = \frac{F}{A}, \text{ where}$$

F is the measured force; A is the original cross-sectional area of the test sample.

The elongation is determined by the formula:

$$\varepsilon = \frac{\Delta L_0}{L_0}, \text{ where}$$

L_0 is measured length of the test sample; ΔL_0 is the length difference from L_0 .

2.3.2. Melt flow index characterization

The melt flow index (MFI) of blend PVA/MTPS was characterized by the extrusion plastometer device (Tinius Olsen, USA) according to the ISO 1133-1:2011. MFI can be calculated by the mass of plastic melted in 10 minutes under the effect of temperature and load. In this study, the temperature was fixed at 190°C, the load was 2.16 kg. All samples were dried at 85°C for 4 hours before analysis.

2.3.3. Scanning electron microscope imaging

To characterize the morphology of specimens, the specimens were coated with a thin layer of platinum (coating 120 seconds) and characterized by scanning electron microscope (SEM, Apreo - ThermoFisher Scientific).

2.3.4. Differential scanning calorimeter analysis

Thermal behavior of the PVA/MTPS blends were determined by using DSC8000 (Perkin Elmer). Heating and colling for both first and second cycles were done in nitrogen atmosphere at the rate of 10°C/min from temperature of 30 to 210°C.

2.3.5. Thermogravimetric analysis (TGA)

Thermogravimetry analyses were carried out by a TGA8000 (Perkin Elmer) instrument. About 10 mg sample was positioned in alunium pans, and the samples were heated at 10 °C/min from room temperature to 600 °C.

III. RESULTS AND DISCUSSIONS

3.1. Effect of plasticizer on 60PVA/40MTPS blend

Blends of PVA/MTPS with a ratio of 60 parts PVA to 40 parts MTPS were prepared by varying the controlled content of plasticizer during the production of MTPS, ranging from 20 to 35 wt% of starch. The mechanical properties of the PVA/MTPS blend were strongly influenced by the amount of plasticizer, regardless of the relative humidity (RH) conditions (Figure 2).

As the plasticizer content increased from 20 to 30 wt%, the tensile strength of the blend showed an improvement. This behavior can be attributed to the plasticizer's effect on the blend. Increasing the plasticizer content enhances the flexibility and molecular mobility of the starch molecules. This, in turn, improves the compatibility between starch and PVA, leading to an enhancement in tensile strength. The increased flexibility allows for better interaction between the polymer chains, resulting in stronger intermolecular forces and improved mechanical properties.

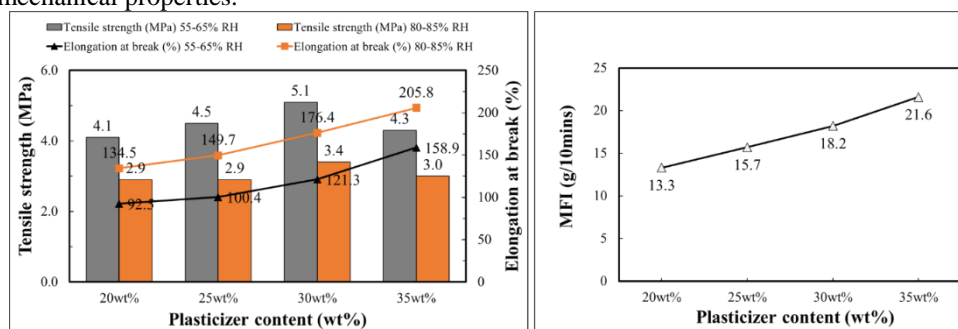


Fig. 2 Effect of plasticizers content on properties of PVA/MTPS blend

However, it is worth noting that there is an upper limit to the beneficial effect of plasticizer content on the blend. When the plasticizer content becomes excessive, around 35 wt%, the flexibility and plasticization of the starch chains reach a point where compatibility is reduced. This decrease in compatibility during the blending process leads to a decline in tensile strength. At this higher plasticizer content, the excessive flexibility of the starch chains disrupts the intermolecular interactions and weakens the overall structure of the blend.

Similarly, the elongation at break of the blend also increased with the plasticizer content. This can be attributed to the enhanced mobility of the polymer chains facilitated by the plasticizer. The addition of plasticizers to polymers increases the flexibility of the polymer chains, allowing them to undergo more deformation before breaking. Consequently, the blend exhibits increased elongation at break as the plasticizer content rises.

To quantify the flowability of the PVA/MTPS blend, the MFI value of each condition was used. increases with the plasticizer content (Figure 2). In the case of the PVA/MTPS blend, it was observed that the MFI increased with the plasticizer content. Specifically, as the plasticizer content increased from 20 to 35%, the MFI value showed a significant increase of 62%, from 13.3 to 21.6g/10mins. This indicates that higher amounts of plasticizer led to improved flow properties and enhanced melt flowability of the blend.

The increase in MFI with higher plasticizer content can be attributed to the plasticizing effect of the plasticizer on the blend. The plasticizer enhances the flexibility and molecular mobility of the starch molecules,

reducing their intermolecular interactions and increasing the fluidity of the polymer melt. This results in easier flow and higher MFI values.

Considering both mechanical properties and the MFI, 30 wt% of plasticizers content was selected for the subsequent experiments.

3.2. Effect of citric acid content on 60PVA/40MTPS blend

3.2.1. Tensile properties and MFI

Effect of citric acid content on PVA/MTPS blend as shown in Table 1

Table 1 Effect of citric acid content on properties of PVA/MTPS blend

Citric acid content (%wt compared to 100% TPS)	MFI (g/10mins)	Tensile strength (MPa)		Elongation at break (%)	
		55-65%RH	80-85% RH	55-65%RH	80-85% RH
0	18.2	5.1	3.4	121.3	176.4
2	12.4	8.9	6.1	175.7	227.3
4	7.1	11.2	9.8	131.7	190.4
6	3.1	The film cannot be blown			

Effect of citric acid content on PVA/MTPS blend as shown in Table 1. Increasing the citric acid content in the materials resulted in a decrease in MFI, indicating reduced flowability. However, it led to a significant increase in tensile strength, with a 120% increase at 55-65% RH and a remarkable 188% increase at 80-85% RH. The addition of citric acid also influenced the elongation at break, which initially increased with citric acid content but dropped back at 4wt%. Moreover, when the citric acid content reached 6wt%, the materials could no longer be blown into a film. These results demonstrate the importance of carefully selecting the citric acid content to achieve the desired properties, considering factors such as flowability, mechanical strength, and processability.

3.2.2. Morphology

In order to understand the impact of PVA/MTPS blend composition on their mechanical properties, we conducted a detailed analysis of their morphology. Scanning Electron Microscopy (SEM) was utilized to examine the surface morphology and internal microstructure of the polymer materials (Figure 3).

In the case of the PVA/MTPS blend alone (Fig. 3a, b), the MTPS particles are observed to form clusters on the surface of the PVA matrix. The distribution of these clusters is uneven, resulting in varying densities and dispersion. The dispersed phase particles exhibit sizes ranging from approximately 20-30µm.

Upon the introduction of citric acid, notable changes in the morphology of the blend can be observed (Fig. 3c, d, e, f). The MTPS particles are now more uniformly distributed and dispersed throughout the PVA matrix. Additionally, the size of the dispersed phase particles appears smaller, measuring around 15-25 µm with 2 wt% CA and 15-20 µm with 4 wt% CA. This indicates that the presence of citric acid promotes improved dispersion and more uniform distribution of the MTPS particles within the PVA matrix.

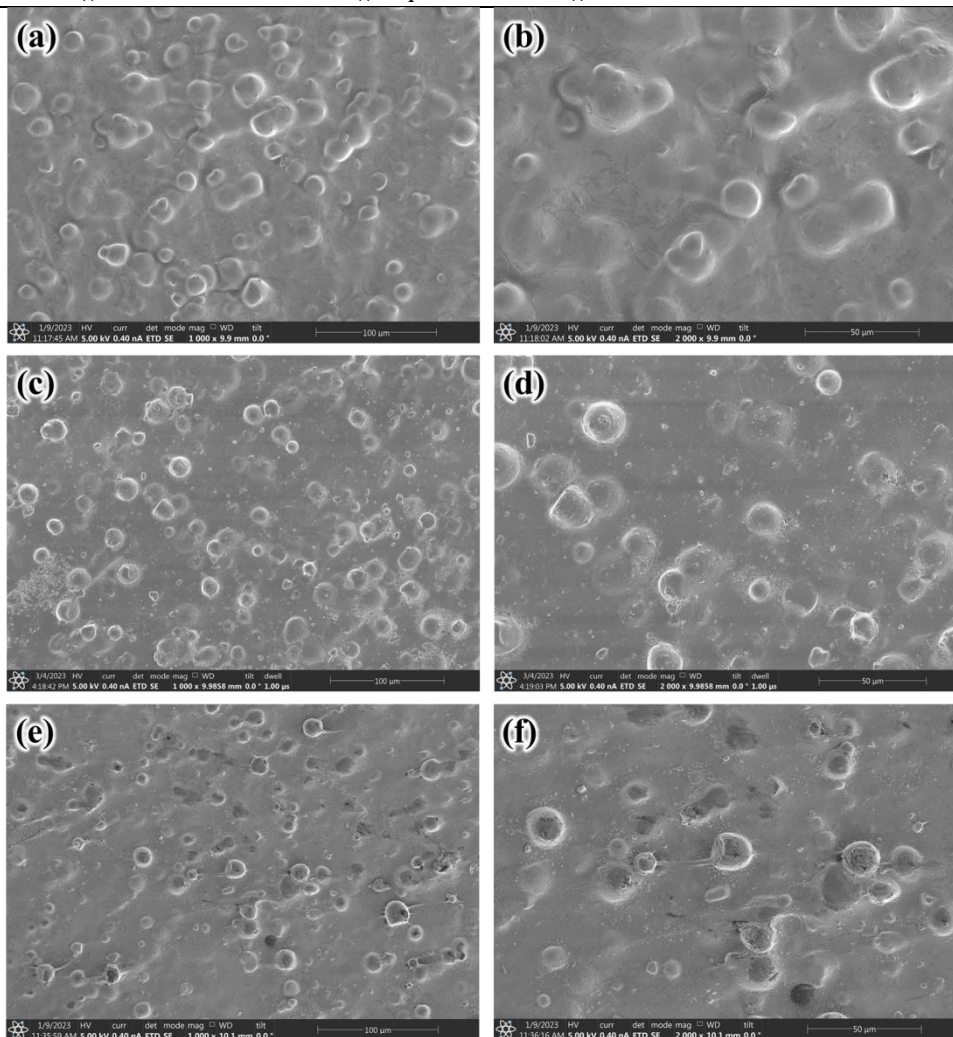


Fig. 3 SEM micrographs of PVA/MTPS (a), (b) PVA/MTPS (60/40); (c), (d) PVA/MTPS (60/40) with 2 wt% citric acid; (e), (f) PVA/MTPS (60/40) with 4 wt% citric acid at 1000x and 2000x magnification

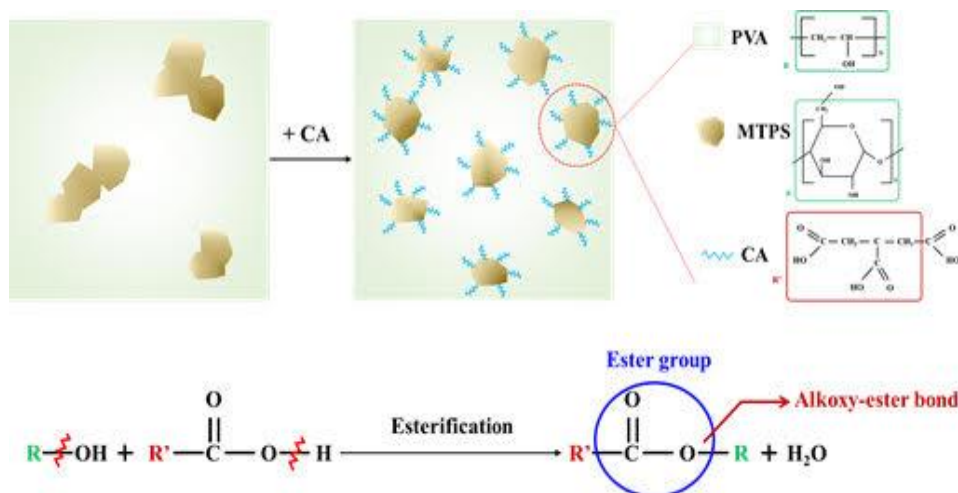


Fig. 4 Breaking mechanism of PVA/MTPS film with and without citric acid

From a chemistry perspective, the use of citric acid as an enhancer in the PVA/MTPS blends involves its interaction with the polymer matrix through various chemical bonding mechanisms. Specifically, citric acid, which is attributed to its ability to form hydrogen bonds with polymer chains. Citric acid contains multiple hydroxyl groups (-OH) and carboxyl groups (-COOH), which can interact with functional groups present in the

polymer matrix. Hydrogen bonding occurs between the hydroxyl and carboxyl groups of citric acid and the polymer chains, leading to increased molecular mobility and flexibility. These hydrogen bonds disrupt the intermolecular forces within the polymer, reducing the stiffness and allowing for easier deformation and improved flow properties. [7,9].

3.2.3. Thermal Properties

We conducted an investigation to assess the effects of citric acid (CA) on the DSC curve of PVA/starch (MTPS) films. The results, which are depicted in Figure 5, suggest that CA has a positive influence on the melting temperature of the films. We observed a slight increase in the melting temperature of PVA/MTPS films as the CA content was raised. Specifically, the melting temperature rose from 188.175°C for films with 0 wt% CA to 195.579°C for films containing 4 wt% CA, as shown in Figure 5a.

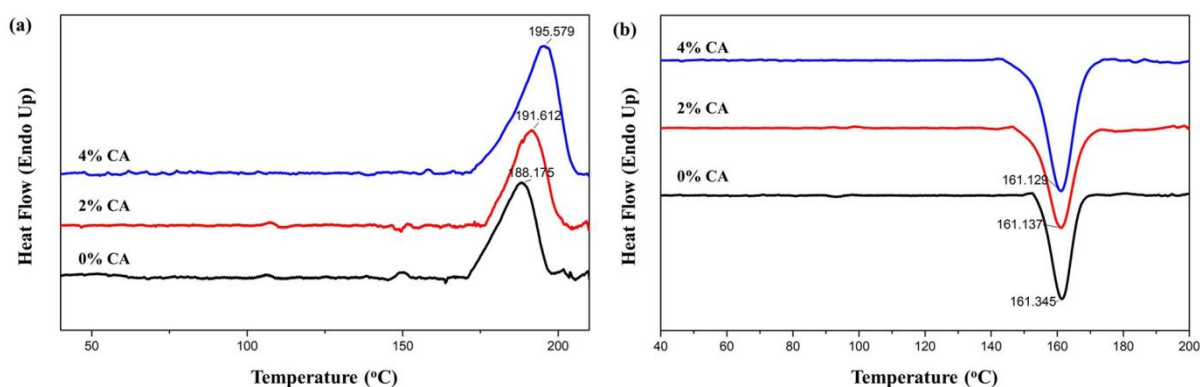


Fig. 5 The effects of citric acid on DSC curve of PVA/MTPS film (a) DSC heating thermograms, (b) DSC cooling thermograms

Interestingly, we found that the presence of CA had minimal impact on the crystallization temperature of PVA/MTPS films. This temperature remained nearly constant at around 161°C, as demonstrated in Figure 5b.

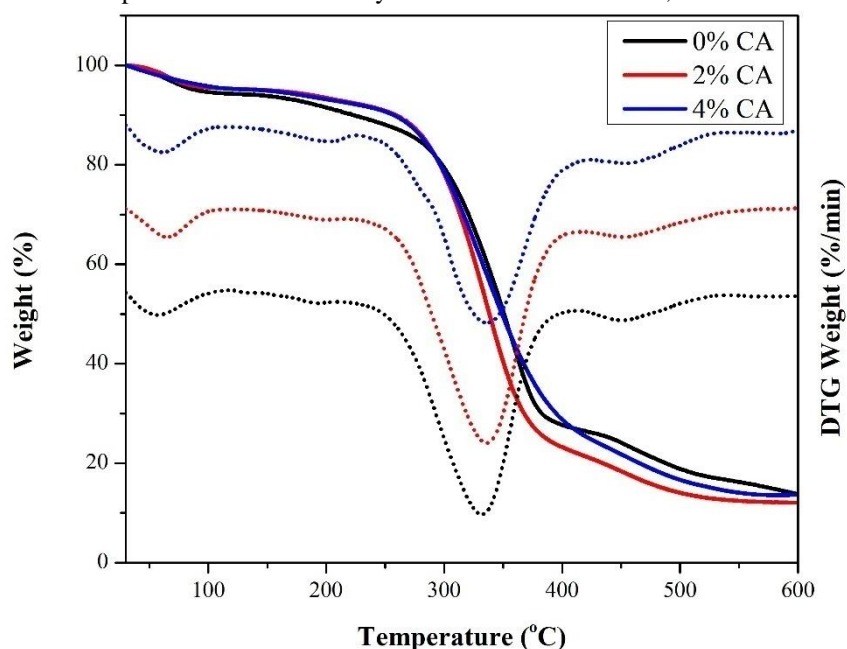


Fig. 6 The effect of citric acid on TG curve of PVA/MTPS films

Moving on to Figure 6, it illustrates the influence of CA on the TG and DTG curve of PVA/MTPS films. The TGA analysis results reveal a three-step decomposition process for the PVA/MTPS film, characterized by three distinct decomposition peaks on the DTG curve. The first step, occurring at around 70 °C, was attributed to the loss of moisture or water.

The second step took place at around 230°C to 420 °C, the PVA/MTPS film experiences its most significant decomposition, centered around 330°C to 345°C. During this stage, involved the heat decomposition of molecules in the PVA/MTPS films, producing small molecular carbon and hydrocarbon. The introduction of citric acid to the blend causes a slight increase in the highest decomposition temperature of the PVA/MTPS film, transitioning from 330°C without CA to 335°C with 2% CA and 345°C with 4% CA. This phenomenon is likely due to citric acid facilitating cross-linking between PVA and MTPS. As the temperature reaches 420°C, the PVA/MTPS decomposes to approximately 73.2% without citric acid, 78.8% with 2 % CA, and 74.6% with 4% CA. Finally, the third step, occurring at approximately 450 °C.

3.3. Effect of MTPS content on PVA/MTPS blend

The observed results in Figure 7 indicate a trend where increasing the MTPS content in the PVA/MTPS blend leads to a decrease in both the tensile strength and elongation at break of the material. Specifically, when the MTPS content increased from 20 to 40wt%, the tensile strength and the elongation at break decreased when evaluated at 55-65% RH and 80-85% RH. Simultaneously, the Melt Flow Index (MFI) slightly increased from 5.8 g/10mins to 7.1 g/10mins, as Figure 7.

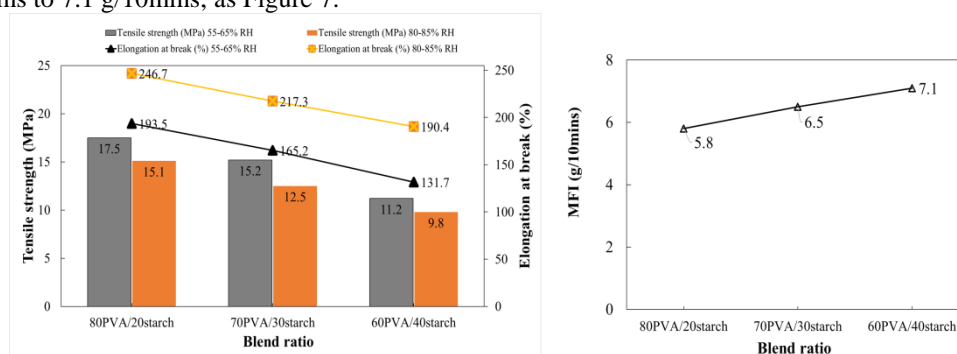


Fig. 7 Effect of starch content on PVA/MTPS blend

These findings highlight the trade-off between MTPS content and mechanical properties in the PVA/MTPS blend. While starch can act as a filler or extender, contributing to cost reduction and potentially improving other aspects of the blend, such as biodegradability, its inclusion in higher proportions can compromise the mechanical strength and elongation properties of the material. Understanding these relationships aids in optimizing the blend composition for specific applications that require a balance between mechanical performance and the desired properties of the starch component.

IV. CONCLUSION

The study achieved the successful preparation of high-performance PVA/MTPS films using blown film extrusion with the incorporation of plasticizer and CA. This combination led to significant changes in the film's properties, particularly in terms of thermal and mechanical characteristics. The esterification reaction between CA and the PVA/MTPS blend played a crucial role in these improvements.

Notably, the melting temperature of the films was enhanced, thanks to the cross-linking effect and the enhanced molecular interactions facilitated by CA. This cross-linking phenomenon had a profound impact on boosting the mechanical properties of the PVA/MTPS films. As the CA content was increased, the mechanical strength of the films exhibited significant improvement, largely attributed to the cross-linking that occurred between CA and the PVA and/or starch components.

The study identified the blend containing 30 wt% plasticizer and 4 wt% CA as the one displaying the most desirable properties. This finding underscores the effectiveness of CA as an additive in optimizing the thermal and mechanical performance of PVA/MTPS films, making them highly promising for a wide array of practical applications.

Overall, the esterification process proved to be a valuable approach for enhancing the properties of the films, rendering them suitable for various uses. The successful incorporation of CA as a key component further highlights the potential of these PVA/MTPS films as high-performance materials with improved thermal stability and mechanical strength.

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