

Original article

Barrier property enhancement of starch citrate bioplastic film by an ammonium-thiourea complex modification

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Abstract

Although **citric acid** modification of starch biopolymers gives a more thermodynamically stable starch citrate, the barrier properties of the product is relatively poor. This paper reports a novel modification process which significantly improved the barrier properties of starch citrate by treating it with a complex formed from ammonium acetate and **thiourea** in the presence of a polysorbate catalyst. The barrier characteristics which were investigated include percentage moisture absorption, percentage reflectance, and water vapour release study. FTIR, SEM and TGA were employed to characterize the starch citrate biofilms before and after ammonium-thiourea complex modifications.

 PreviousNext 

Keywords

Bioplastics; Starch citrate; Barrier properties; Thiourea; Biopolymers

1. Introduction

Sustainable chemistry is the branch of chemistry which substitutes the usage of synthetic and less environmental friendly polymers with natural, biodegradable and ecofriendly biopolymers [1]. Biodegradable packaging materials which can be obtained from renewable materials like **cellulose**, poly(lactic acid), starch, poly(hydroxyalkanoates) etc. [2] have been applied as materials which can develop barriers to gases, moisture and even microorganisms especially in their modified forms [3]. Different post-modification processes can make starch or cellulose very useful as packaging materials with good barrier properties.

Starch has been applied in its granular, gelatinized and plasticized form as packaging films, delivery films, biodegradable containers, stabilizers, industrial and engineering adhesives etc. [2]. Till today, the fabrication of starch biopolymer into packaging plastics with favourable and durable mechanical, thermal and barrier properties remains somehow difficult [4]. Several literatures contain reports on synthesis of films from **polysaccharides**, proteins, lipids and their composites with other synthetic polymers like **polyimides**, **polyethers** and epoxy resins with acceptable plastic characteristics [5], [6]. However, biopolymer chemists and technologists are still finding answers to the production of starch based bioplastic with excellent barrier properties through physical and chemical modifications [7].

One of the most environmental friendly ways to modify starch bioplastic from the literature is through **citric acid** treatment which has been found to improve thermodynamic stability of starch [8], [9]. The interactions between the carboxylic structures of citric acid and hydroxylic structures of starch creates a more tightly held starch citrate thereby making citric acid a good crosslinking agent for starch biopolymers [10].

Starch citrate is attracting more interest for industrial applications due to its thermodynamic stability and relative hydrophobic performance. The major challenge with starch citrate is its barrier characteristics which are relatively poor [11], [12]. Food packages which are starch citrate or xanthate based tend to lose their barrier properties within a short period of time. This is due to the fact that as starch citrate is exposed and heated up over time, citric acid switches from its function as a crosslinker to a plasticizer [13]. The plasticizing effect reduces the bond adhesions and the inherent barrier property in citric acid modified starch biopolymers over time [11].

Starch biopolymers with good barrier properties can find application in plastic, films and foams industries [14]. Several biopolymers with good barrier properties also have good optical applications in transparent packaging materials (for fruits, vegetables and eggs), lens products and laminates [7]. The significant methods of improving the barrier properties of ordinary starch or starch citrate include cross-linking with oxazoline derivatives, treatment with oils and resins, blending with poly(alkyl acrylate) derivatives, poly(acrylonitrile) and poly(hydroxyalkanoates) derivatives [15], [16], [21]. The set-back involved is the issue of compatibility between the hydrophobic oils, acrylates and acrylonitriles. A new in-situ method of improving the barrier property of starch and starch citrate through intra-molecular binding between a complex of ammonium acetate and **thiourea** is reported in this paper.

2. Materials and methods

2.1. Materials

Potato starch, citric acid, ethanol, ammonium acetate, thiourea and tween 80 were all analytical grade and obtained from Sigma Aldrich, USA

2.2. Preparation of starch citrate

The preparation of starch citrate was based on the method of Chang et al. [17] with some modifications. Potato starch (20 g) was added to 200 mL of distilled water and heated at 90 °C for 30 min under constant stirring in a reaction vessel. The resulting slurry was freeze-dried for 5 days to facilitate gelation. Ethanol was used to dissolve citric acid and disperse porous starch powder. The suspension was then conditioned for 16 h at room temperature and afterwards washed with ethanol to remove excess citric acid [18]. The citric acid plasticized starch was later cast into films and air dried.

2.3. Ammonium-thiourea modification of starch citrate

Ammonium acetate (0.77 g) and 0.76 g of thiourea was dissolved in 100 mL of water, 10 g of the prepared starch citrate was then dispersed in the solution. The mixture was heated at 80 °C with vigorous stirring for 60 min and 3 drops of tween 80 was added 10 min after heating.

2.4. Water vapour release study

The ASTM dry cup method and the method of Mali et al. [19] was adopted and slightly modified. Cups with specific diameters and depths were fitly covered with the various starch films (unmodified and modified) with 2 g of anhydrous CaSO₄ (Relative Humidity of 0%) in each cups. Each cup was placed in a desiccator conditioned at 97% relative humidity using K₂SO₄ and were weighed at various time intervals. The water vapour release study was done using the mass changes of the cups.

2.5. Moisture absorption

The procedure of Angles and Dufrense [20] was used. Dried films of the ordinary starch, starch citrate and the ammonium-thiourea starch citrate with 3 cm by 5 cm were conditioned to 0% relative humidity using CaSO₄ and weighed. The same films were conditioned to 55% relative humidity in a desiccator using KNO₃ and re-weighed at different time intervals.

2.6. Characterization

The functional groups present in the ordinary starch, starch citrate and thiourea modified starch citrate were investigated using Agilent Micro lab PC technologies from 450 to 4000 cm⁻¹. The scanning electron microscope of Phenom ProX, USA was used to analyze the surface morphology of the starch citrate and thiourea modified starch citrate. Weight changes with respect to temperature of both modified starches were analyzed using Pelkin Elmer thermal analysis instrument. The heating was carried out in the range of from 45 to 950 °C at 10 °C/min and the initial decomposition temperatures were obtained from the thermograms directly.

3. Results and discussions

Citric acid is one of the well known cross-linking agent for improving the general strength and performance of biopolymers. Fig. 1 shows the cross-linking modification of starch with citric acid via the C6-OH and C2-OH of the starch macromolecules through proton abstraction from the respective carbon centres. The cross-linking helps to create more covalent citrate ester bonds and also improves the number of mobile chains within the starch molecule [5].

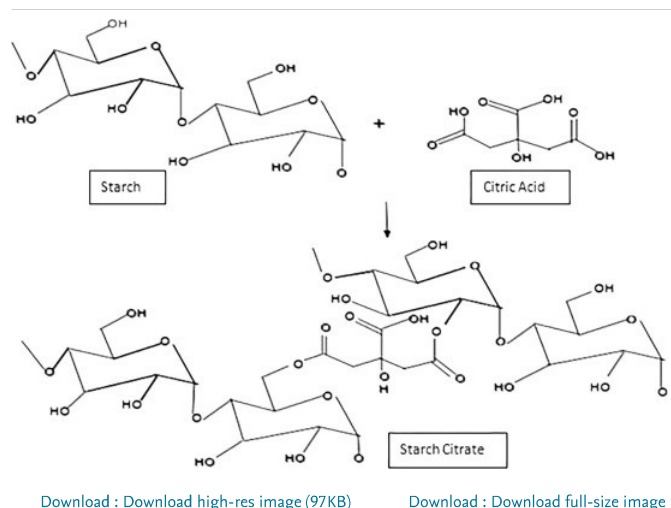


Fig. 1. Reaction scheme for starch citrate formation.

Fig. 2 reveals how the ammonium-thiourea is incorporated into the starch citrate macromolecular structure. Ammonium ion tends to suppress the overall pH of the system so as to presumably give room for the elimination of the hydroxyl group on the C-6 of the amylopectin portion of the starch biopolymer. In general, the ammonium acetate-thiourea complex modified starch citrate is more flexible than the starch citrate and the ordinary starch because of the additional effect of polysorbate (tween 80) treatment.

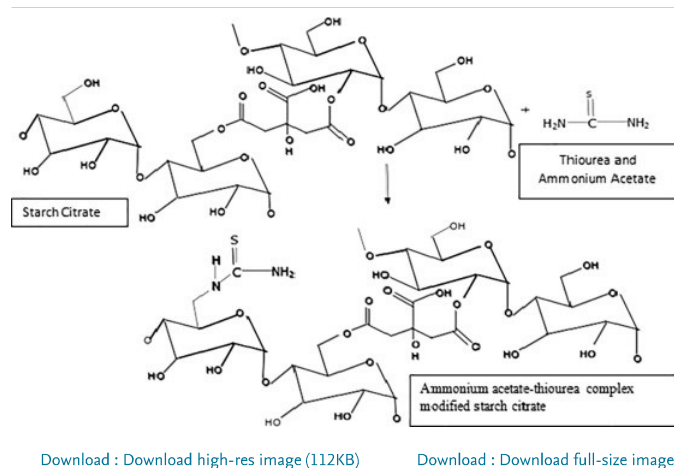


Fig. 2. Reaction scheme for the modification of starch citrate with [thiourea](#) and ammonium acetate.

3.1. Water vapour release study

The experimental water vapour release study helps to understand the barrier behavior of films and membranes by estimating the amount of water vapour that can pass through the pores and boundary surface of bio-polymeric films [19]. Fig. 3 shows the amount of water vapour released (in grams) from ordinary starch, starch citrate and ammonium-thiourea modified starch citrate with respect to different time ranges. The mass of water vapour ranged from 0.362 to 0.784 g in starch, 0.318 to 0.616 g in starch citrate and 0.208 to 0.443 g in ammonium-thiourea modified starch citrate. Generally, films with low water vapour release profile have better barrier properties and good packaging applications [8].

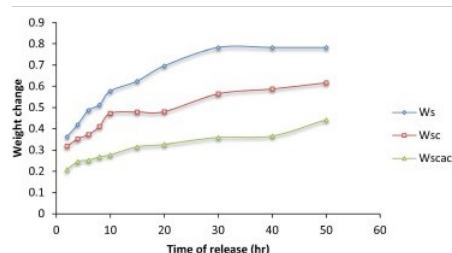


Fig. 3. Water vapour release study of starch, starch citrate and ammonium acetate-thiourea complex modified starch citrate.

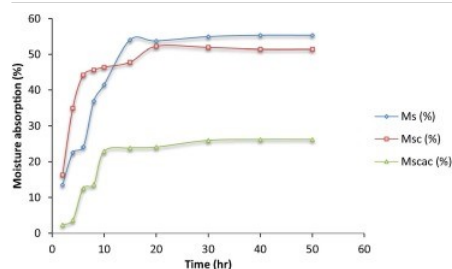
From Fig. 3, a high gradient was observed for the release of water vapour for the first ten hours for the starch and starch citrate while the release rate in ammonium-thiourea modified starch citrate had a moderate gradient which signifies a more controlled release property as a result of the [thiourea](#) modification. Another high rate of release around 20–30 h for starch and starch citrate further reveals their poor barrier characteristic and release profile. The thiourea modified starch showed a generally even gradient in the water vapour release and also released the lowest amount of water vapour (up to a 50% reduction when compared with that of ordinary starch).

Although the hydrophobic ester groups in starch citrate crosslink the starch and introduce new intramolecular bonds thereby reducing the amount of water vapour that can be released in starch, the thiourea further entangles the internal polymeric chains of the modified starch, increase the water resistibility, reduces the water vapour release ability and improves overall boundary properties [21].

3.2. Moisture absorption

The moisture absorbed by a material can also be used as an index of its barrier property. The presence of citrate esters in starch blocks the free spaces thereby reducing the moisture absorbing ability, whereas the modification with thiourea further creates more intramolecular bonds and block the free points of attachment for water molecules [17].

From a general overview of the graph in Fig. 4, the amount of water absorbed (in percentage) for the ammonium-thiourea modified starch (Mscac) is less than 60% of water absorbed by the starch (Ms) and starch citrate (Msc) after 8 h. In addition, this absorption values for the thiourea modified starch citrate is gradually adjusted to about half of the moisture absorption capacity displayed by the ordinary starch and starch citrate at longer durations (>10 h).



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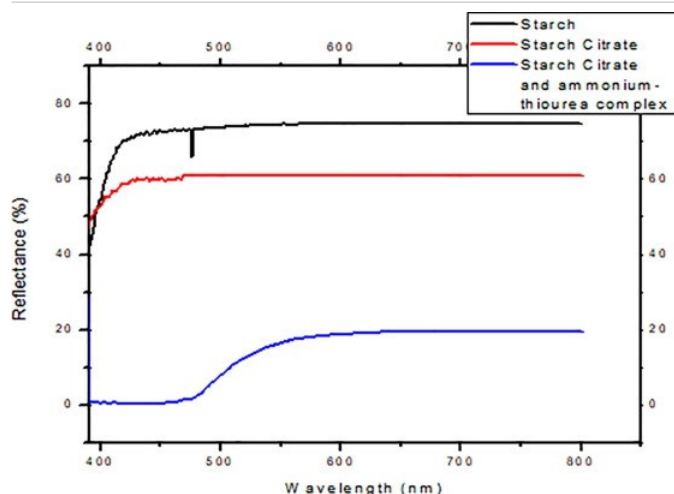
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Fig. 4. Moisture absorption of starch, starch citrate and ammonium acetate-thiourea complex modified starch citrate.

The points with very high gradients on the graph indicate the period of rapid moisture absorption; the rate of moisture intake is more than the rate of water entanglement to the inner structural spaces. Since the ammonium-thiourea modified starch had the lowest moisture absorption property, it can be very useful in the storage of fruits and vegetable products due to the fact that it does not absorb the essential water content of these fruits and vegetables thereby preserving their freshness.

3.3. Reflectance property

The reflectivity and emissivity of barrier materials should be low [8]. The surprisingly low reflectance value of ammonium-thiourea modified starch citrate biopolymer is presumably due to the assembly pattern of the thiourea and citrate pendants on the starch biopolymer. The reflectance was lower than 2 at wavelength below 500 nm; although the reflectance moved to 20 at longer wavelength of 600 nm and above, its reflectance values across the wavelengths were much lower than that of the ordinary starch and starch citrate (Fig. 5).



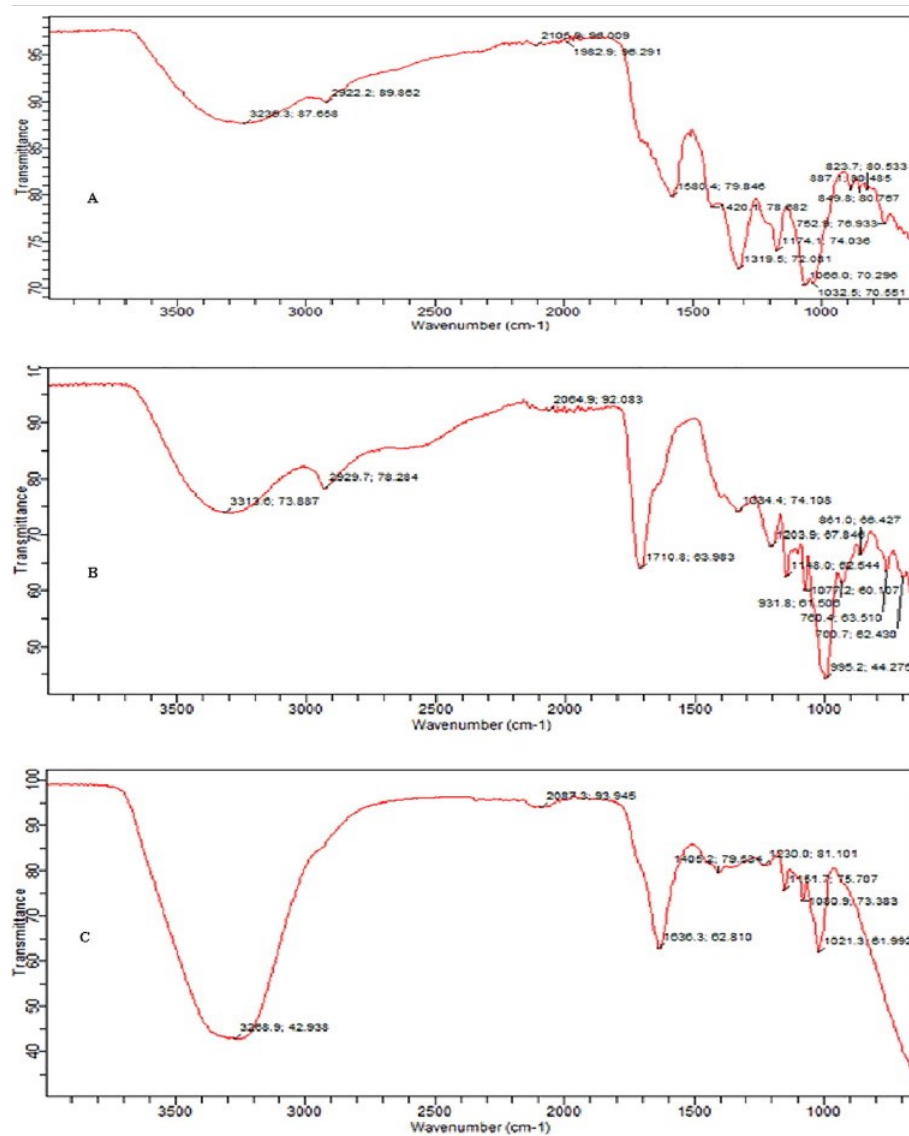
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Fig. 5. Reflectance of starch, starch citrate and ammonium acetate-thiourea complex modified starch citrate.

3.4. FTIR analyses

Fig. 6a–c shows the FTIR analysis of starch, starch citrate and ammonium acetate-thiourea complex modified starch citrate. The presence of O—H, C—H and glycosidic C—O—C at 3238, 1066 and 2922 cm^{-1} confirms the functional groups of starch biopolymer. The transmittance peak at 3318 cm^{-1} is attributed to the O—H group of the starch citrate while the peak at 2629 cm^{-1} is the CH of a glucopyranose ring. The peak at 1148 cm^{-1} is the transmittance peak of C—O bond stretching of C—O—H groups in the anhydroglucose ring. The 1020 cm^{-1} is attributed to C—O of C—O—C group. The transmittance peak due to the stretching C=O was observed at 1710 cm^{-1} . This confirms the formation of citrate esters between the hydroxyl groups in starch and the carboxylic anhydride group in the citric acid [18].



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Fig. 6. (A–C) FTIR of ammonium acetate-thiourea complex modified starch citrate.

The peak at 1230 cm⁻¹ is attributed to C—N bond stretching of C—N—H group. The bending vibration for O—H and N—H were respectively seen at 1405 and 1379 cm⁻¹ while the C=S bond stretching was seen at 2087 cm⁻¹ and the C=O at 1710 cm⁻¹ for citrate modified was shifted to 1636 cm⁻¹. The reduction in the peak intensity of the ammonium-thiourea modified explains the creation of new intramolecular hydrogen bonding between the hydroxyl groups of the starch and the nitrogen complex (Fig. 7).

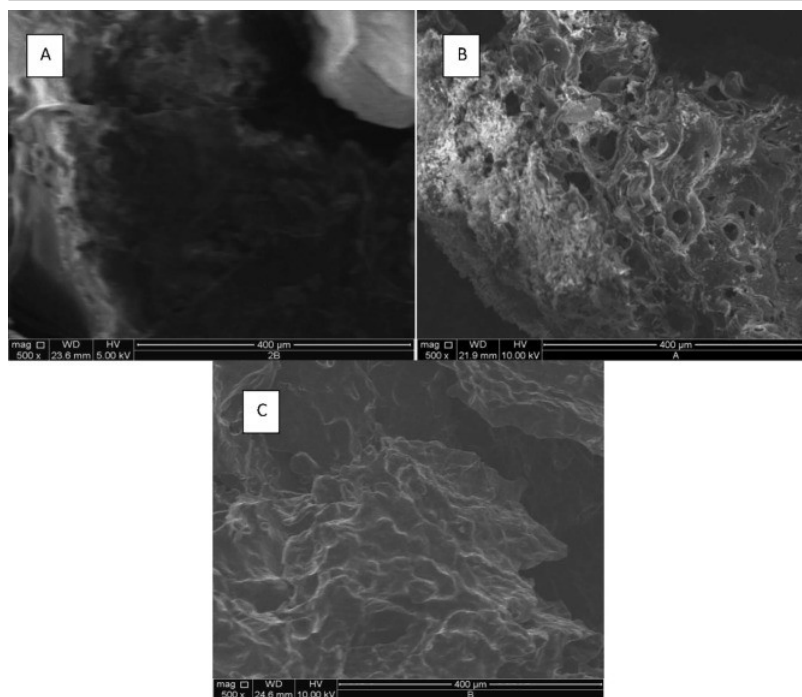
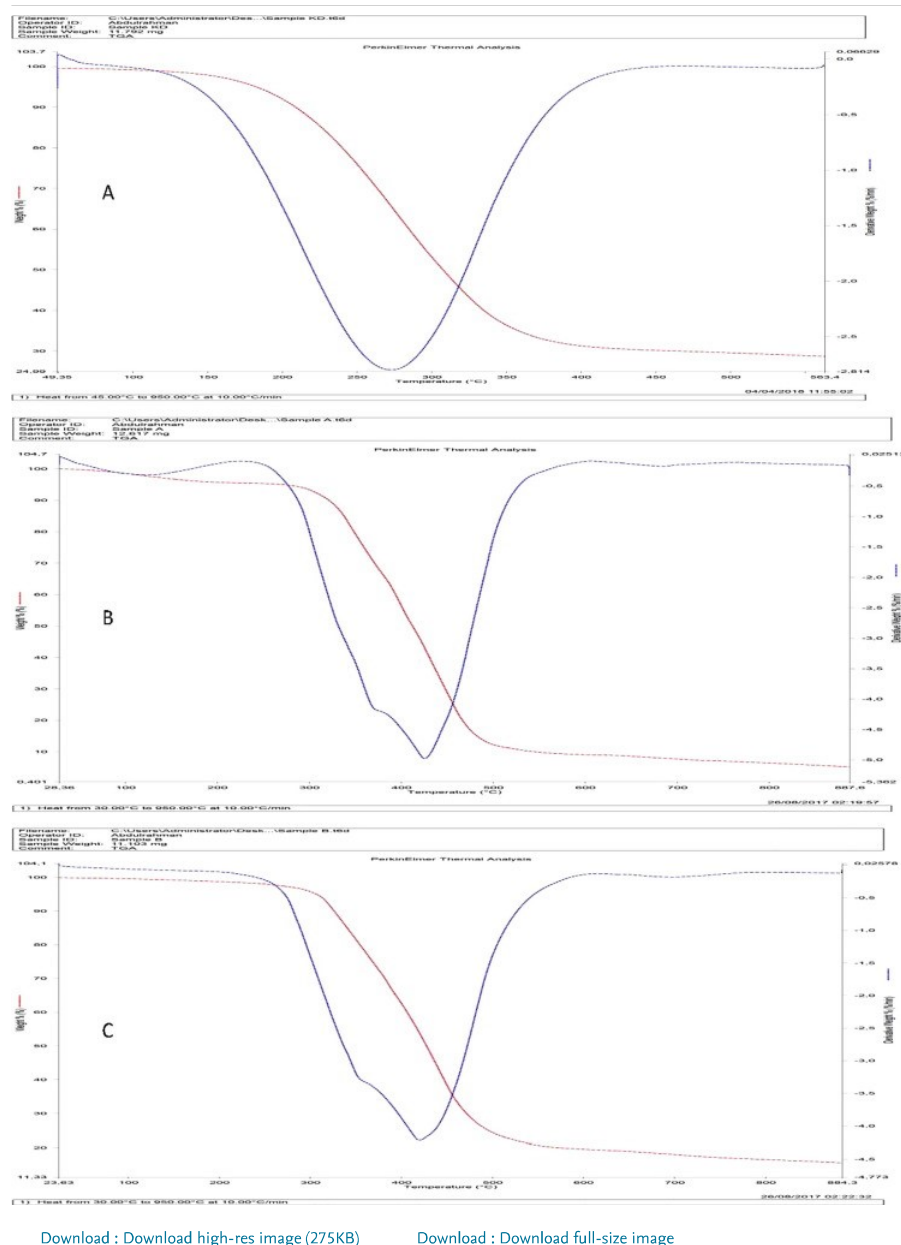
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Fig. 7. (A–C) SEM of starch, starch citrate and ammonium acetate-thiourea complex modified starch citrate.

3.5. Scanning electron microscopy

The Fig. 8 shows the SEM images of the starch, starch citrate and the ammonium-thiourea modified form and provides information about the overall surface characteristics of the biopolymers under no fracture. The starch has a gel-like and partially smooth surface [16]. The SEM of starch citrate reveals a non-uniform compact structure with some parts having a porous and spongy like appearance while other parts have compact appearance because regions where citrate groups are situated within the starch citrate biopolymer have surrounding negative charges which tend to open up more spaces within the structure through repulsion. The starch citrate exhibited irregular pore arrangement at the porous region. This explains why it is not suitable for use as a durable barrier material.



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Fig. 8. (A–C) TGA of ammonium acetate-thiourea complex modified starch citrate.

The SEM image of the ammonium-thiourea modified starch citrate revealed a well aligned arrangement of the starch structure and disappearance of most of the pores. It shows a high level of compactness and a regular surface morphology. The alternative ridge-like surface appearance explains the reason for its low reflectance and confirms it can be further processed for better bioplastic applications [23].

3.6. Thermogravimetric analyses

In order to investigate the thermal properties of the starch, starch citrate and ammonium-thiourea modified starch citrate polymers, they were characterized using TGA. The starch biopolymer passed through a critical mass loss stage from 220 to 330 °C leading to 83% mass loss. The observed value for thermal decomposition for the ordinary starch is 280 °C. For starch citrate, the TGA as seen in Fig. 8 shows a two-step thermal degradation in which the first minor degradation might be as a result of the decomposition of glucans, amylopectins, and other relatively soluble macromolecules in the starch citrate [22], [24]. It was observed that there was mass loss from 320 °C to 465 °C leading to 70% weight loss. The initial observed value for thermal decomposition (T_{onset}) for porous starch citrate was marked at 420 °C.

TGA characterisation as in seen in Fig. 8 showed that the initial thermal decomposition value (T_{onset}) for ammonium-thiourea modified porous starch citrate was 423 °C with mass loss observed from 335 °C to 460 °C leading to 53% mass loss. The TGA characterization shows that ammonium-thiourea modification of starch increases the thermal stability of porous starch citrate, as the value for percentage mass lost in ammonium-thiourea modified starch (53%) is lower than that of porous starch citrate (70%).

4. Conclusion

This study has shown that the barrier properties of starch citrate can be improved by treating it with ammonium acetate and thiourea. Reflectivity study shows that ammonium-thiourea modified starch citrate film has low reflectance properties. TGA analysis indicates that it has a better thermal stability compared to that of porous starch citrate. Comparative water vapour release and moisture absorption studies of ordinary starch, starch citrate and ammonium-thiourea

modified starch citrate revealed that ammonium-thiourea modified starch citrate film performed better as barrier against water vapour and moisture.

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