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Enhancing the functional properties of acetylated hemicellulose films for active food packaging using acetylated nanocellulose reinforcement and polycaprolactone coating

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ABSTRACT

Acetylated hemicellulose (AH)-nanocellulose (ACNC) films coated with polycaprolactone (PCL) films, were evaluated as active packaging for aqueous, alcoholic, fatty and acidic food. The effects of nanocellulose loading (0–50 %), degree of acetylation (DS) (0–2.34) and polycaprolactone coating (0.3 g/mL) on hydrophobicity and solubility of AH films in food simulants, were investigated. In addition, AH-CNC/PCL films were doped with polyphenols and their antioxidant release (temperature 5 °C–40 °C, time - 48 h) into food simulants was evaluated experimentally and by modelling (Migratest software). Increasing ACNC DS and loading, combined with a PCL coating increased films' hydrophobicity (24.59° to 82.48°) and reduced film solubility in all the simulants (~82.8 %). The release of polyphenols by the films was highest and best predicted using Migratest software for the fatty food simulant. Therefore, these films can be used as active packaging for fatty foods. Furthermore, Migratest modelling can be used to predict film performance during film design.

1. Introduction

In recent years, several studies have focused on finding alternative raw materials for developing food packaging films to replace the non-degradable petroleum-based packaging material. Hemicellulose has gained attention as a possible substitute for synthetic packaging material such as low density polyethylene (LDPE) (Li & Pan, 2018; Peng, Peng, Xu, & Sun, 2012). However, the utilisation of hemicellulose-based films as food packaging material is limited to dry foods due to the high solubility of hemicellulose in wet food media. Modification processes such as benzylation, fluorination and acetylation have been attempted to forge hydrophobicity in hemicellulose, with the aim of widening the application of hemicellulose films (Chen et al., 2014; Farhat et al., 2017; Xu et al., 2008). Among the aforementioned strategies applied to minimise the solubility of hemicellulose-based films in food media, acetylation is considered the safest and most efficient method for modifying polymers for food packaging material development (Egüés, Stepan, Eceiza, & Toriz, 2014).

In order to further improve the hydrophobicity of AH films, ACNC is added as a reinforcing material (Gordobil, Egüés, Urruzola, & Labidi, 2014). Research on the development of AH films reinforced with ACNC is still limited to the blending of AH with ACNC that has a DS of 0 and 0.54 (Gordobil et al., 2014). However, there is potential in further enhancing the hydrophobicity of AH films by reinforcing them with ACNC that has a DS above 0.5. Increasing the DS of ACNC reduces the number of hydroxyl groups in the film, available for hydrogen bonding with water, while increasing hydrophobic acetyl groups (Akkus, Ozkan, & Bakir, 2018; Ayoub, Venditti, Pawlak, Sadeghifar, & Salam, 2013). The hydrophobic groups act as a barrier to the penetration of moisture through the film (Khodaeimehr, Peighambardoust, & Peighambardoust, 2018), hence, inhibiting the accumulation of water in the film (Ayoub et al., 2013). In addition, reinforcing the AH films with higher quantities of hydrophobic fillers, can reduce the film surface area available to bond with water molecules (Siracusa et al., 2018). Thus, increasing the DS and loading of ACNC in AH films, can be a strategy in developing films with enhanced water barrier properties. The ACNC subsequently enhances the mechanical properties of the AH films (Gordobil et al., 2014).

AH-ACNC films have been recommended for food packaging, based on the barrier properties (oxygen barrier, gas barrier) and mechanical properties (Young modulus and tensile strength) without testing their stability when in contact with food media (Farhat et al., 2016). Solubility testing of packaging material in aqueous, acidic, alcoholic and fatty food simulants is among the recognised approaches to evaluate the stability of packaging material when in contact with different food media (EU, 2011; Sanches Silva, Cruz, Sendón García, Franz, & Paseiro

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Losada, 2007). This test procedure has been done on both biopolymers and synthetic-based films. Examples of the films include: pectin-carboxyl methylcellulose films, starch triacetate films, LDPE and Ethylene vinyl alcohol (Fang & Vitrac, 2017; García Ibarra, Sendón, García-Fonte, Paseiro Losada, & Rodríguez Bernaldo de Quirós, 2019; Traistaru, Rivis, Moldovan, & Menelaou, 2013; Yu, Hu, & Wang, 2017; Zhu, Li, Huang, Chen, & Li, 2014). Biobased films are water soluble, hence they disintegrate when exposed to food containing water. The dissolution of the film in food can affect the integrity of the film and the quality of the packaged food (Bhunia, Sablani, Tang, & Rasco, 2013). Furthermore, the dissolved packaging material components can be a health hazard to consumers when in concentrations above the allowable limit (Gavriil, Kanavouras, & Coutelieris, 2018). Thus, the assessment of the solubility of the AH-ACNC film in food is necessary.

Recent developments in food packaging materials include the production of films capable of releasing active compounds into packaged food (active packaging) to increase food shelf life (Cesur, Köroğlu, & Yalçin, 2017; Muriel-Galet, Cran, Bigger, Hernández-Muñoz, & Gavara, 2015). The active compounds eliminate oxidising agents (for example free radicals) and microorganisms (for example bacteria) responsible for food spoilage, thereby, prolonging food shelf life (Ebrahimi, Peighambardoust, Peighambardoust, & Karkaj, 2019). Natural antioxidants such as tea polyphenols, tocopherol, and anthocyanins have been incorporated into both synthetic (LDPE) and biobased polymers (starch, pectin), and the release of these antioxidants into food was experimentally and theoretically assessed (López de Dicastillo, Bustos, Guarda, & Galotto, 2016; Pereira, de Arruda, & Stefani, 2015). Theoretical evaluation of antioxidant release by packaging material is often done using software packages such as AKTS SML and Migratest EXP, which were developed based on Fick's second law of diffusion. The predictions made by the aforementioned softwares are compared to experimental data to assess whether these models can be used for packaging material design (Duan, Chen, Zhu, Zhang, & Zhang, 2013; Poças, Oliveira, Oliveira, & Hogg, 2008).

More importantly, it is crucial that active packaging materials have controlled release of antioxidants into food with time, so as to minimise the accumulation of antioxidants in food at the same time facilitating the removal of food spoilage agents as they are generated (Uzunlu & Niranjan, 2017). Antioxidant concentration beyond the allowable limit (60 mg/kg of food) in food can be a health hazard to consumers (EU, 2011). A coating can be applied to food packaging material to control the migration of antioxidants into food, thereby, ensuring a slow release of antioxidants from packaging materials (Yu et al., 2017). Polymer coatings such as polycaprolactone (PCL), have been applied to packaging to prevent the direct contact of the packaging material with food as well as to increase the distance which the entrapped active compounds have to travel to reach the surface of the food, thus, facilitating a slow release of the entrapped bioactive agents into food (Ali Akbari Ghavimi, Ebrahimzadeh, Solati-Hashjin, & Abu Osman, 2015). In addition, coatings having been reported to minimise film solubility and improve both the surface properties and mechanical properties of packaging material (Maciel, Yoshida, & Franco, 2014; Rešček et al., 2018). Therefore, there is potential in developing AH-ACNC based active packaging with controlled release capabilities, and enhanced mechanical and barrier properties, by coating the films with PCL.

The controlled release of chemicals from hemicellulose-based material has only been tested with dry food. Previous research has investigated the utilisation of a hemicellulose coating to prevent the papermaking residual chemicals in recycled paper from migrating into tenax, a dry food simulant. Depending on the surface charge of the chemicals, the hemicellulose chelated some of the chemicals, thus, restricting their migration into the food (Grondahl et al., 2013). However, the ability of hemicellulose-based films, particularly the acetylated hemicellulose films, to encapsulate and release antioxidants into wet food, has not yet been evaluated. Therefore, in order to diversify the application of the hemicellulose-based films, it is necessary to investigate the antioxidant release by the hemicellulose-based films in different wet food environments (acidic, aqueous, alcoholic and fatty food), to ascertain the film behaviour in these environments.

The overall objective of the study was to develop AH-based active packaging films and test their application as a packaging material for wet foods. The effects of increasing ACNC DS beyond 0.54, ACNC loading (10 %–50 %) and applying a PCL coating on the AH-ACNC film's hydrophobicity (water contact angle (WCA), mechanical properties (Young modulus, tensile strength and percent elongation), and solubility in food simulants (aqueous, acidic, alcoholic and fatty), were investigated. LDPE films were used as a benchmark. In addition, the ability of AH-based films to entrap and release bioactive compounds (mango peel polyphenols) into food simulants, was investigated both experimentally and by modelling, using Migratest Exp software.

2. Materials and methods

2.1. Chemicals

Sodium hydroxide (NaOH), ethanol, sulphuric acid, hydrochloric acid (HCl), phenolphthalein indicator and sodium carbonate were sourced from Kimix Chemical & Lab Supplies (Cape Town, South Africa), and carbazole, glucuronic acid, acetic anhydride, acetic acid, dimethyl sulfoxide (DMSO), sugar standards (arabinose and xylose), gallic acid, Folin Ciocalteu reagent, dichloromethane, polycaprolactone (PCL) (molecular weight 80 000), and 1-diphenyl-2-picrylhydrazyl (DPPH) were purchased from Sigma Aldrich (Germany). University of Maine, Orono, U.S.A supplied the freeze-dried nanocellulose. LDPE crystals were sourced from Sasol (South Africa). All the chemicals were of analytical grade. Wheat straw was obtained from wheat straw farmers in Cape Town, South Africa.

2.2. Sample preparation

2.2.1. Hemicellulose extraction and acetylation

Wheat straw was milled to a particle size of 80-mesh using a Retch ZM200 mill. Thereafter, the wheat straw was sieved to remove the oversized and fine particles according to the British Standard Sieving Test Procedure, BS 410. The wheat straw was then stored in a dry place until the commencement of the experiments.

Wheat straw was delignified prior to hemicellulose extraction. The delignification process involved reacting 200 g of wheat straw with 2 L of 1 % NaOH/50 % ethanol solution. Delignification was carried out in schott bottles by incubating the reaction mixture in a shaking water bath at 75 °C for 6 h. The solid residue remaining after delignification was washed three times with (1 L) water to remove the black liquor. Thereafter, the residue was oven dried at 40 °C to a moisture content of less than 10 %. Hemicellulose was then extracted from the delignified wheat straw (80 g) with 10 % NaOH (800 mL) at a solid/liquid ratio of 1:10. The reaction was carried out in schott bottles incubated in a shaking water bath set at 25 °C for 24 h. A hemicellulose rich supernatant was recovered by vacuum filtration (45-μm filter paper supplied by Lasec, South Africa). The supernatant was neutralised to a pH of 5.5 with 10 % HCl before dialysis (cellulose dialysis tube membrane with a molecular weight cut off of 14 000, Sigma Aldrich, Germany) to remove salts. Hemicellulose was then recovered by centrifuging the dialysate at 8 000 rpm for 30 min. Subsequently, the hemicellulose was dried to a moisture content of < 10 % using an oven set at 40 °C for three days. The recovered hemicellulose had a uronic acid content of 8.91 %, lignin content of 4.6 % and an arabinose/xylose ratio of 0.087.

Hemicellulose was acetylated according to a method developed by Belmokaddem, Pinel, Huber, Petit-Conil, and Da Silva Perez (2011), with modifications; sulphuric acid was used as a catalyst for the acetylation process instead of methanesulfonic acid. A gram of hemicellulose was thoroughly mixed with 2.5 mL of 99 % acetic acid in a schott bottle. The reaction mixture was placed in a water bath set at

50 °C for 5 min. The mixture was then cooled to 25 °C in an ice bath before 6.6 mL acetic anhydride/ 200 µL 98 % sulphuric acid was added. Acetylation was carried out in a shaking water bath maintained at 50 °C for 1 h. After acetylation, the AH was precipitated with 150 mL of 95 % ethanol. Residual acetylation reagents were removed by washing the AH four times with 100 mL of 95 % ethanol. AH was then oven dried for 24 h at 40 °C.

2.2.2. Nanocellulose acetylation

Nanocellulose was acetylated based on a procedure reported by Sahlin (2015). Approximately, 3 mL of 99 % acetic acid was added to 300 mg of nanocellulose and the mixture thoroughly mixed for 1 min. Subsequently, a solution of 1 mL of 99 % acetic anhydride and 1 µl of 98 % sulphuric acid was added to the nanocellulose/acetic acid mixture. The reaction was performed in 50 mL falcon tubes incubated in a water bath set at 25 °C. Nanocellulose was acetylated to different degrees of acetylation by varying the acetylation time from 10 min to 240 min. After acetylation, 150 mL of water was added to the mixture to stop the reaction and to precipitate the ACNC. ACNC was washed three times with 150 mL of water to remove residual acetylation chemicals. The ACNC was then oven dried at 40 °C for 24 h

2.3. Preparation of hemicellulose films

The hemicellulose-based films were prepared according to a method highlighted by Egüés et al. (2014). AH-ACNC films reinforced with ACNC of different DS were prepared by dissolving 375 mg of AH and 125 mg ACNC in 20 mL of DMSO by heating for 6 h at 50 °C in a shaking water bath. AH-ACNC films with different ACNC loading were formulated by dissolving concentrations of ACNC ranging from 10 % to 50 % (based on the total film solids weight, 500 mg), together with AH in 20 mL of DMSO. The mixture was heated in a water bath at 50 °C for 6 h. The hemicellulose-based films were then created by solvent casting the homogenous mixture in 80 mm glass petri dishes before oven-drying at 50 °C for two days (Egüés et al., 2014). A coating of PCL on the AH-ACNC films and AH-ACNC-Polyphenol films was formed by dipping films in 100 mL of 0.03 g/mL PCL/dichloromethane solution for 5 s. No polyphenols were added to the PCL coating. The coated films were then oven-dried at 25 °C for 24 h. Film thickness was measured using an Elcometer (model 456CFSS). The thickness of the films was controlled by maintaining the quantity of film mixture and size of petri dish used for solvent casting.

2.4. Preparation of low density polyethylene films

LDPE films were developed by injection moulding (Thermo scientific Haake mini Jet II from Lasec, South Africa). The injection and mould temperature were set at 130 °C and 100 °C respectively. The moulding was carried out at 450 bars for 20 min.

2.5. Analytical methods for determining the physicochemical properties of hemicellulose, nanocellulose and hemicellulose-based films

2.5.1. Determination of the degree of acetylation of hemicellulose and nanocellulose

The AH and ACNC were analysed for the acetylation DS according to the method reported by Gordobil et al. (2014) with slight modifications (0.1 M solutions of NaOH and HCl were used for titration instead of the 0.5 M used in the original method). The acetylated samples (200 mg) and unmodified (blank) samples (200 mg) were added to 10 mL of 75 % ethanol and incubated in a shaking water bath for 30 min at a temperature of 50 °C. The reaction was carried out in schott bottles. Thereafter, the mixture was allowed to cool to 25 °C in an ice bath. Approximately, 10 mL of 0.1 M NaOH was added to the mixture, prior to titrating the mixture to the phenolphthalein endpoint with 0.1 M HCl. Further titration of the mixture was carried out after 2 h to neutralise any excess alkali released by the sample. The acetyl content of the hemicellulose and nanocellulose was determined using Eq. (1).

$$Acetyl\ content\ (\%) = \frac{(V_a - V_b) \times N_{hcl} \times M_{acetyl}}{M_s} \times 100 \quad (1)$$

where V_a is the titer volume for the blank in litres, V_b is the titer volume for the acetylated sample in litres, N_{hcl} is the molarity of the HCl, M_{acetyl} is the molecular weight of the acetyl groups, 43 g/mol, M_s is the weight of the samples in grams used in the analysis

The DS of the AH and ACNC was calculated based on Eq. (2):

$$Degree\ of\ substitution = \frac{Acetyl\ content \times 162}{[(M_{acetyl} \times 100) - (M_{acetyl} - 1)] \times Acetyl\ content} \times 100 \quad (2)$$

2.5.2. Determination of water contact angle of acetylated hemicellulose-based films

A stereomicroscope (Nikon SMZ-2 T, Japan) that has a camera, was used to determine the WCA of the AH-based films. The procedure involved placing 1 µL droplets of deionised water onto the film surface and capturing the images of the droplets. Scion Image software was then used to measure the contact angle of the droplets on the film surface.

2.6. Determination of the functional properties of acetylated hemicellulose-based films

2.6.1. Assessment of film solubility in the food simulants

The solubility of AH-ACNC films in the aqueous (deionised water), acidic (3 % acetic acid), alcoholic (10 % ethanol) and fatty (95 % ethanol) food simulants, was determined according to a method stated by López De Dicastillo et al. (2011). The AH-ACNC films, cut into strips with a length and width of 2 cm x 2 cm, were totally immersed in food simulants (30 mL) for 24 h at 25 °C. After that the strips were oven dried at 40 °C for 24 h. The solubility of the film was calculated as the percentage weight of the film that dissolved in the simulant after 24 h.

2.6.2. Determination of antioxidant release by the acetylated hemicellulose-based films

A mango peel polyphenol extract, with total polyphenol content of 82.04 mg/g Gallic acid equivalent (GAE) and antioxidant activity of 93.4 %, was used as the antioxidant source. AH-ACNC-Polyphenol/PCL were developed by immersing the AH-ACNC film in the polyphenol extract for 1 min. The films were then allowed to dry in an oven for 1 day at 25 °C. The films were able to absorb 2.89 mg/g GAE of the mango polyphenols (0.057 mg/cm^2). A PCL coating was applied to the films using the procedure described in Section 2.3.

The film polyphenol release into the food simulants was determined according to a method formulated by Yu et al. (2017). Strips of the AH-ACNC-Polyphenol/PCL films, with length and width of 2 cm, were immersed in 30 mL of food simulant and incubated at 5 °C, 25 °C and 40 °C for 48 h. A sample of the simulant was taken periodically to analyse polyphenol content and antioxidant activity based on the method highlighted by Ribeiro, Barbosa, Queiroz, Knödler, & Schieber (2008). The polyphenol content of the simulant was determined using the Folin Ciocalteu reagent. Approximately 0.5 mL of the Folin Ciocalteu reagent and 0.5 mL of 7.5 % sodium carbonate were added to 0.5 mL of the food simulant and the mixture was allowed to react in the dark for 30 min. The reaction was carried out in falcon tubes incubated in a fume hood at 25 °C. Absorbance of the mixture was read on a Varian Cary 50 Bio UV visible (UV-VIS) spectrophotometer at a wavelength of 765 nm. A gallic acid calibration curve was used to quantify the polyphenols in the simulant.

The antioxidant activity of the simulant was determined using the DPPH scavenging method. Approximately 100 µL of the simulant was

mixed with 5 mL of 0.1 mM DPPH in plastic tubes wrapped with aluminium foil. The mixture was allowed to react for 30 min in a fume hood at 25 °C before its absorbance was read on a Varian Cary 50 Bio UV visible (UV-VIS) spectrophotometer at a wavelength of 517 nm. The antioxidant activity was calculated as the percentage absorbance difference between the absorbance of the simulant mixed with the reagents and the absorbance of the reagents only.

2.7. Modelling the release of mango polyphenols by the acetylated hemicellulose-based films into the food simulants

The migration of mango peel polyphenols from the AH-ACNC-Polyphenol/PCL films into food simulants was modelled using Migratest EXP software. Migratest EXP software predicts the migration of chemicals from packaging material into food using Ficks' second law of diffusion, (Eq. 3), (Gavriil et al., 2018).

$$\frac{\partial C_A^P}{\partial t} = D_A^P \frac{\partial^2 C_A^P}{\partial x^2} \tag{3}$$

where C_A^P is the concentration of migrant type A from the packaging film, P. D_A^P is the diffusion coefficient of the migrant, and t and x are the time and distance the migrant travels through the packaging material into the food simulant respectively. The diffusion coefficients of the polyphenols encapsulated by the hemicellulose-based films were calculated using Eq. (4) (Yu et al., 2017).

$$D = \left(\frac{kL_P}{4}\right)^2 \pi \tag{4}$$

where D is the diffusion coefficient, L_P was calculated as half of the film thickness. k is the gradient of the graph, $\frac{M_{F,t}}{M_{F,\infty}}$, $M_{F,t}$ is the amount of mango polyphenols migrating into the simulant at a specific time and $M_{F,\infty}$ is the maximum quantity of mango polyphenols that migrated into the simulants after 2 days.

The partition coefficients of the films were calculated based on Eq. (5).

$$K_P = \left(\frac{C_P}{C_S}\right) \tag{5}$$

where K_P is the partition coefficient, C_P is the concentration of the mango polyphenols remaining in the hemicellulose-based film after 2 days, and C_s is the concentration of mango polyphenols that migrated into the simulant after two days.

The polyphenol release by the AH-ACNC-Polyphenol films was modelled for the temperatures of 5 °C, 25 °C and 40 °C, and time ranging from 0 h to 48 h. Migration modelling was carried out for the aqueous, acidic, alcoholic and fatty simulants. The simulant volume was specified as 30 mL. The AH-ACNC-Polyphenol/PCL film length, width and thickness were 2 cm x 2 cm x 0.0358 cm. The films were specified as having three layers, namely, the AH-ACNC layer with a thickness of 0.250 mm and a PCL layer with a thickness of 0.054 mm on either side of the AH-ACNC layer. PCL density was stated as 1.45 g/cm^3 and the density of AH-ACNC films, 0.785 g/cm^3, was experimentally calculated from the densities of AH and ACNC. The mango polyphenols molecular weight (300.07) was calculated, based on method reported by Shivapuji (2019), considering the molecular weights and composition of the individual polyphenol type present in the mango peel polyphenol extract.

2.8. Imaging of hemicellulose-based films using field emission scanning electron microscopy

Images of the hemicellulose-based films were captured using a Carl Zeiss Merlin FESEM equipped with a GEMINI II column. The films were first coated with gold and secured on a stub using double sided tape, prior to imaging. Then an in-lens detector set at working distance = 4.5 mm, probe = 100 Pa and EHT = 3.00 kV, was used to capture the film images. Imagej software was used to analyse the SEM images to determine the dispersibility of ACNC in AH films.

2.9. Structural characterisation of hemicellulose-based films using Fourier transform infrared spectroscopy (FTIR)

The structural characteristics of hemicellulose-based films were analysed using a Nexus model FTIR spectrometer fitted with a Golden Gate diamond single reflectance ATR sampling accessory (Thermo Scientific, Nicolet, USA). The hemicellulose-based films absorbance was measured within the wavelength range of 650 to 4000 cm^{-1}, at a resolution of 8 cm^{-1} after performing 64 co-added scans. The FTIR spectra were produced using the Origin 6 software (OriginLab cooperation, USA).

2.10. Statistical analysis

All analysis was carried out in triplicate. Comparison of the means of the results was performed using the Duncan multiple stage analysis in Statistica version 7, 13.2 software.

3. Results and discussions

3.1. Effect of nanocellulose degree of substitution on acetylated hemicellulose/nanocellulose film thickness

Acetylation of nanocellulose resulted in ACNC with DS ranging from 0 to 2.34 and the means of the DS were significantly different ($p < 0.05$) from each other (Table S1). The nanocellulose DS had an effect on the thicknesses of the AH-ACNC films, that is, the film thickness decreased from 81.47 to 53 μm upon increasing the DS of the reinforcing ACNC from 0 to 2.34 (Table S1). This could be due to the DS of the ACNC affecting the dispersion of ACNC in the film matrix, as evidenced by a decline in distance between the ACNC particles in the film from 447.71 nm to 6.35 nm when ACNC DS decreased from 2.34 to 0 (Table S2, Fig. S1). At a lower DS, the ACNC particles entangled and agglomerated, compromising the dispersion of the ACNC in the AH matrix (Table S2) (Dong, Yan, Jin, & Li, 2017; Fasihnia, Peighambardoust, & Peighambardoust, 2017), thereby, increasing film thickness and reducing the uniformity of the films (Table S1).

3.2. Effect of nanocellulose degree of substitution on acetylated hemicellulose film hydrophobicity and solubility in food simulants

Reinforcing AH (DS 1.7) with ACNC of higher DS (increasing DS from 0 to 2.34), reduced the solubility of the hemicellulose-based films, from 30.88 % to 16.30 %, in the food simulants (Fig. 1a). The observed trend can be attributed to the reduction in the hydroxyl group content of the films when the ACNC DS increased. Replacing the hydroxyl groups in the nanocellulose with hydrophobic acetyl groups, limits hydrogen bonding of the films with water, thereby, reducing the solubility of the film in food simulants (Fang, Sun, Tomkinson, & Fowler, 2000). Furthermore, the acetyl groups of the ACNC form strong hydrophobic networks with acetyl groups in AH which restrict water absorption and film swelling when in water-based simulants, thus, reducing the solubility of the film into the simulant (Fortunati et al., 2012). Films reinforced with ACNC that has a low DS are likely to form hydrogen bonds with water in simulants because of the high hydroxyl groups content, thus, promoting the dissolution of the films in simulants (López De Dicastillo et al., 2011). The films were generally least soluble in the fatty food simulant when compared to the other simulants because the fatty food simulant has a lower water content (5 %) than the other simulants (90–100 %) (Fig. 2a). Hence the fatty food simulant has a lower concentration of hydroxyl groups available for bonding with the films than the other simulants (Fortunati et al., 2012). Therefore, AH films reinforced with ACNC have potential application as packaging

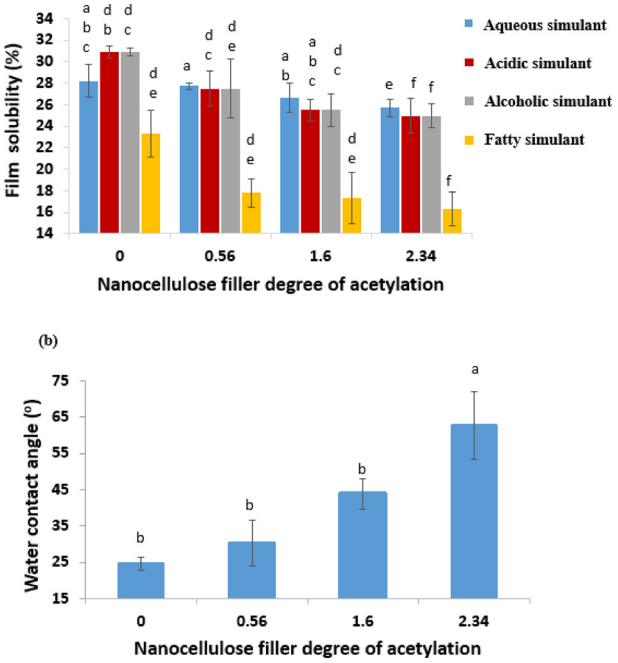

Fig. 1. Hemicellulose-based film (a) solubility in food simulants and (b) water contact angle as affected by varying the degree of acetylation of the reinforcing nanocellulose. The values are means of three measurements. Values with different letters are significantly different ($p < 0.05$). The error bars represent standard deviation.

material for fatty foods when compared to the aqueous, alcoholic and acidic food.

A significant reduction ($p < 0.05$), of up to 38.16 %, in solubility of AH based films in all the food simulants was observed when the DS of the reinforcing ACNC was increased from 1.6 to 2.34 (Fig. 1a). The results suggest that the compatibility of the AH matrix and the ACNC filler was boosted by the DS of nanocellulose (Dong et al., 2017; Fortunati et al., 2012). On the other hand, there was no significant reduction ($p > 0.05$) in the solubility of AH-ACNC films when the DS of ACNC increased from 0 to 1.6 (Fig. 1a). The phenomenon suggests that there is a minimum DS in nanocellulose which inhibits the solubility of AH-ACNC films in the simulants. Most likely, for such low DS, the hydrophobic networks present in the films were not sufficient to prevent the films from forming hydrogen bonding with water in the simulants. Nevertheless, the AH-ACNC films reinforced with ACNC of DS ranging from 0 to 1.6, exhibited functional properties suitable for packaging fatty foods as evidenced by the least solubility of these films into the fatty simulant when compared to the aqueous, alcoholic and acidic food simulants (Fig. 1a).

The hydrophobicity of the AH-ACNC films was enhanced by increasing the DS of the ACNC reinforcement as evidenced by the increase in WCA of the films from 24.59° to 62.68° as the nanocellulose DS increased from 0 to 2.34 (Fig. 1b). The AH films containing ACNC with DS 2.34 had a WCA significantly higher ($p < 0.05$) than that of AH films reinforced with ACNC which had DS ranging from 0 to 1.6.

These results are supported by other researchers who reported that the hydrophobicity of hemicellulose films can be enhanced by incorporating hydrophobic fillers (Fortunati et al., 2012; Gordobil et al., 2014). However, the WCA of the films reinforced with ACNC of DS ranging from 0 to 1.6 were statistically the same ($p > 0.05$), suggesting that this acetylation DS range was not sufficient to cause a significant increase in the hydrophobicity of the films. Therefore, the

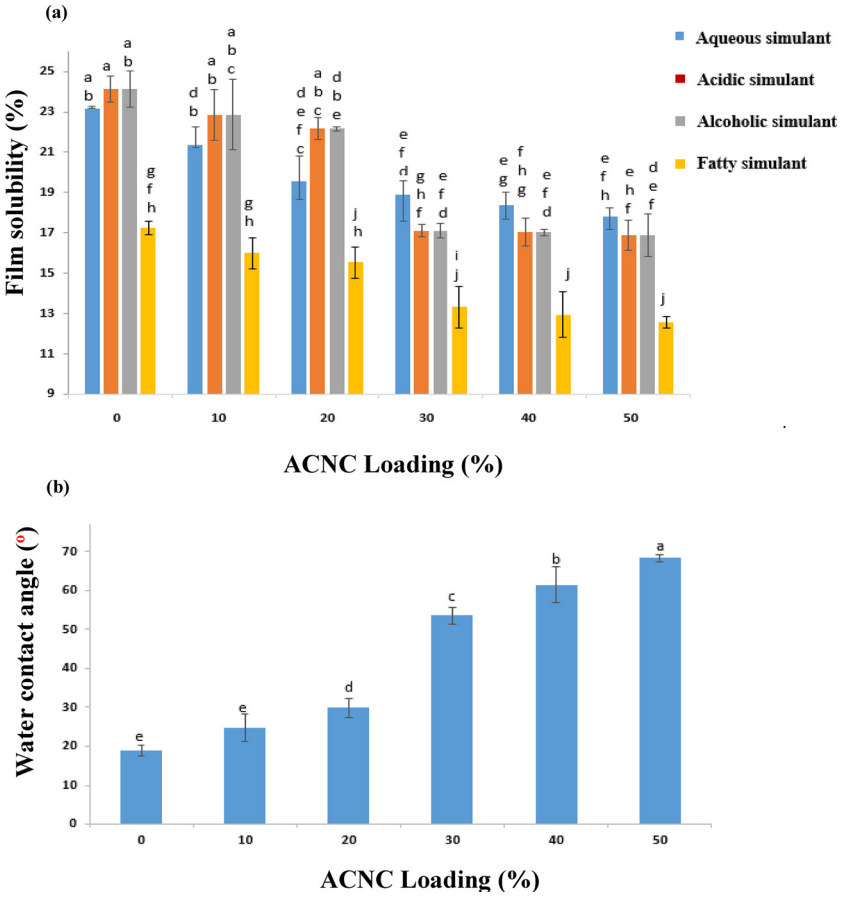

Fig. 2. Hemicellulose-based films (a) solubility in food simulants, (b) water contact angle as affected by varying the reinforcing acetylated nanocellulose loading. The values are the means of three measurements. Values with different letters are significantly different ($p < 0.05$). The error bars represent standard deviation. The ACNC loading is the weight percent of nanocellulose in the film.

phenomenon of increasing the hydrophobicity of AH-based films by the addition of ACNC would only apply when the minimum DS has been achieved, which in this case should be greater than 1.6. In addition, other factors such as dispersion, loading and compatibility of the reinforcing material and the matrix play a role in the overall hydrophobicity of the biocomposites (Mehdikhani, Gorbatikh, Verpoest, & Lomov, 2019).

3.3. Effect of nanocellulose loading on acetylated hemicellulose film hydrophobicity and solubility in food simulants

Increasing the ACNC (DS 2.34) loading from 10 % to 50 % in AH films (DS 1.7) led to a reduction in solubility of the films in the food simulants, from 24.12 % to 12.57 % (Fig. 2a). The observed results can be attributed to an increase in the formation of hydrophobic bonds between hemicellulose and nanocellulose, as nanocellulose loading increased, leading to the creation of hemicellulose-nanocellulose networks which shielded the hydroxyl groups in the film from interacting with the simulant (Huang et al., 2018). In addition, regardless of the ACNC loading, the acetylated hemicellulose films were least soluble (as low as 12.57 %) in the fatty food simulant when compared to the other simulants (Fig. 2a).

An improvement in hydrophobicity of the AH-ACNC films, depicted by an increase in WCA from 18.97 to 68.29°, was realised when the ACNC loading increased from 10 % to 50 % (Fig. 2b). The increase in hydrophobicity of the films can be attributed to the reduction in film surface area available for hydrogen bonding with water as the quantity of ACNC in the hemicellulose matrix increased. Peighambardoust, Peighambardoust, Pournasir, and Mohammadzadeh Pakdel (2019)) highlighted that the inclusion of a more hydrophobic filler in a film matrix enhances the hydrophobicity of the film. Similar results were reported by Pereira et al. (2014), when they observed that increasing nanocellulose loading in Polyvinyl alcohol composites improved the WCA. Therefore, ACNC loading is an important factor that can be manipulated when aiming at developing AH-ACNC films with improved moisture barrier properties.

3.4. Effect of polycaprolactone coating, acetylated nanocellulose and polyphenols on the mechanical and functional properties of acetylated hemicellulose-based films

The tensile strength of AH-ACNC based films was similar to that of LDPE films ($p > 0.05$). (Table 1). However, the Young modulus of the AH-ACNC films was higher than that of LDPE by 58.6 % (Table 1). On the other hand, the percent elongation of the AH-ACNC (15.49 %) (Table 1) and WCA (68.29°) could not match those of the LDPE (percent elongation of 1621.22 % and WCA of 84.91°) (Table 1). Thus, reinforcing AH with ACNC alone is not enough to develop AH-based films that have all the functional properties similar to LDPE films (Table 1).

A PCL coating further improved the hydrophobicity of the AH-ACNC films from 68.29° to 82.48°. The PCL is inherently hydrophobic (82.91°), thus, its use as a coating improved the water barrier properties of the AH-ACNC films (Zhou, Bayati, & Choi, 2013). However, there was no significant difference ($p < 0.05$) in the tensile strength and elongation between the PCL coated AH-ACNC films and the uncoated AH-ACNC films (Table 1).

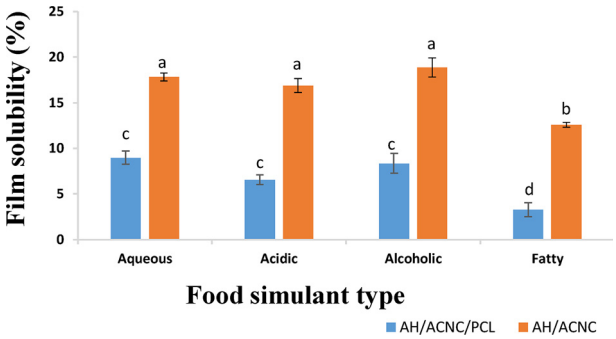

Fig. 3. Solubility of acetylated hemicellulose-based films, with and without a coating of polycaprolactone, in food simulants. The values are means of three measurements. Values with different letters are significantly different ($p < 0.05$). The error bars represent standard deviation.

The lower Young modulus of PCL (280.30 MPa) when compared to AH-ACNC films (590.15 MPa) led to a significant reduction ($p < 0.05$) in the Young modulus of the coated AH-ACNC films (335.33 MPa) (Table 1). Consequently, the coating resulted in a AH-ACNC film with a Young modulus closer to that of the LDPE films (244.46 MPa).

The PCL coated films had lower solubility in food simulants when compared to uncoated films (Fig. 3). The PCL coating prevented the direct contact of AH-ACNC with the food simulants, thereby, reducing the dissolution of the films in the simulants. PCL is insoluble in food simulants (Shen, Hu, Wang, & Zhou, 2015), therefore, the solubilisation of the coated films in the simulants is evidence that the coating layer was porous. Furthermore, the SEM images, shown in Table S3, support this fact, as pores can be seen on the surface of the AH-ACNC/PCL films. The reduced solubility of the film and porosity of the PCL layer can be exploited for development of AH-ACNC/PCL films with controlled and slow release of antioxidants.

The addition of polyphenols to the AH-ACNC/PCL films had no effect on the mechanical properties of the films ($p > 0.05$) but led to a reduction in the hydrophobicity of the films by 29.32 % (Table 1). The increase in film hydrophilicity upon incorporating polyphenols may be due to the high water affinity of the mango polyphenols. In the presence of moisture, the hydroxyl groups of the polyphenols form hydrogen bonds with water molecules, thereby, reducing the WCA of the films (López De Dicastillo et al., 2011). Fasihnia, Peighambardoust, Peighambardoust, and Oromiehie (2018) support these findings when they reported a decline in water barrier properties of polypropylene films upon adding sorbic acid. Based on the fact that the moisture barrier properties of the films were compromised by the inclusion of polyphenols, the AH-ACNC/PCL films are most suitable for packaging

Table 1
Comparison of mechanical properties and hydrophobicity of acetylated hemicellulose-based films with polycaprolactone films and low density polyethylene films.

Film type	Young Modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Water contact angle (°)	Film thickness (mm)
PCL	$280.30^{bc} \pm 52.28$	$13.61^{a} \pm 2.25$	$43.90^{a} \pm 1.76$	$82.91^{a} \pm 0.46$	0.560 ± 0.031
AH-ACNC	$590.15^{a} \pm 95.86$	$10.59^{ab} \pm 1.24$	$15.49^{a} \pm 3.19$	$68.29^{b} \pm 0.81$	0.250 ± 0.045
AH-ACNC/PCL	$335.33^{bc} \pm 21.14$	$6.72^{b} \pm 0.65$	$16.01^{a} \pm 2.01$	$82.48^{a} \pm 6.73$	0.4345 ± 0.082
AH-ACNC-Polyphenols/PCL	$409.91^{c} \pm 14.46$	$8.47^{ab} \pm 1.44$	$15.75^{a} \pm 0.13$	$63.78^{b} \pm 4.48$	0.3585 ± 0.024
LDPE 1	$244.46^{b} \pm 63.51$	$11.07^{ab} \pm 3.97$	$1621.22^{b} \pm 597.02$	$84.91^{a} \pm 2.28$	0.044 ± 0.0035
LDPE 2	$220.41^{b} \pm 46.56$	$14.98^{a} \pm 1.70$	$200.02^{c} \pm 46.72$	$86.1^{a} \pm 0.75$	0.486 ± 0.011

The values are the means of three measurements. Values with different letters are significantly different ($p < 0.05$) from each other. LDPE 1 is a commercial LDPE film and LDPE 2 was experimentally developed. PCL: Polycaprolactone, AH: Acetylated hemicellulose, ACNC: Acetylated nanocellulose, LDPE: Low density polyethylene.

oily or fatty foods. Fatty foods have little or no moisture hence, a packaging with lower hydrophobicity may be suitable for containment of such food. However, the major drawback of using these films is that they may allow moisture from the environment to come into contact with the packaged fatty foods, thus promoting oxidation processes, and thereby, compromising food shelf life (Samsudin, Soto-Valdez, & Auras, 2014). However, the polyphenols in these films should be able to minimise the oxidation of the fatty foods and prevent food spoilage.

3.4.1. Hemicellulose-based films as active food packaging material

The polyphenol release by the AH-ACNC-Polyphenol films into the food simulants was dependent on the food simulant type, time and temperature (Fig. 3). The polyphenol content of all food simulants increased when temperature was increased from 5 °C to 40 °C and time from 0 h to 48 h. These results were in agreement with the antioxidant release profiles of polylactic acid films reported by Jamshidian, Tehrany, & Desobry (2013). A food packaging material capable of releasing antioxidants into food when food storage temperature deviates is important during food transportation. Normally, during transportation, food may be exposed to changes in temperatures and it could be hours before realising that food quality has been compromised (Biji, Ravishankar, Mohan, & Srinivasa Gopal, 2015). Hence, an active packaging material capable of releasing antioxidants in response to temperature can minimise temperature dependent microbial growth and oxidation processes, thereby, preventing food spoilage (Cesur et al., 2017). The response of the AH-ACNC-Polyphenol/PCL films to temperature and time is an indication that these films may be suitable for utilisation as active food packaging material.

The highest polyphenol release by the films was into the fatty food simulant at 40 °C (Fig. 3) followed by the alcoholic simulant and lastly the aqueous and acidic simulant. Fortunati et al. (2012) reported that there are two mechanisms responsible for antioxidant release by polymer matrices namely the swelling of polymers and solubilisation of antioxidants in the food simulant. The swelling of the polymer film when in contact with food simulants results in voids that act as passageways through which the antioxidants diffuse out of the film into the simulant, thus, promoting polyphenol release. In addition, the rate of release of polyphenols by polymers is boosted by the high solubility rates of polyphenols in the food simulant (Fortunati et al., 2012). In this study, the highest polyphenol release was into the fatty simulant, a food media in which AH-ACNC/PCL films were least soluble (Fig. 3). Furthermore, mango polyphenols are known to be highly soluble in ethanolic solutions, that is why these solutions are normally used for polyphenol extraction (Ajila, Bhat, & Prasada Rao, 2007; Geerkens, Matejka, Schweiggert, Kammerer, & Carle, 2015). This implies that the higher solubility of the polyphenols in the fatty simulant (95 % ethanol) than in the other simulants (with high water content 90–100 %), was the major contributing factor to the release of polyphenol by the films. Therefore, the AH-ACNC films prepared in this study are most suitable for packaging fat-rich foods.

3.4.2. Comparison of model predictions and experimental results of the polyphenol release by acetylated hemicellulose-based films

The experimental and model data for polyphenol release by the hemicellulose-based films into food simulants and the resultant antioxidant activity of the food simulant are shown in Figs. 4 and 5. The fitted curve model equations for the polyphenol release and antioxidant activity experimental data are highlighted in the supplementary information (Table S4 and Table S5). The polyphenol release by the AH-ACNC-Polyphenol/PCL films, into all simulants, in response to temperature and time, followed a logarithmic trend. The Migratest models were capable of predicting the release of mango polyphenols by the films into the food simulants within the first 5 h (Fig. 4). The predicted polyphenol release deviated from the experimental results as the film-simulant contact time increased from 5 h to 48 h. The deviation can be due to the changes in the structure of the films as the polyphenols are released and partly because of the dissolution of the film matrix in the food simulants (Samsudin et al., 2014). The structural changes are not accounted for during migration modelling using Migratest software, hence, the differences in the model predicted values and the experimental results.

Migration modelling using Migratest EXP software provides reliable predictions for the polyphenol release by the AH-ACNC/PCL films into the fatty food simulant, as shown by the close fitting of the model to the experimental data (Fig. 4b). The model, overestimated the release of the polyphenols from the films (Fig. 4b and d) into the fatty and acidic simulant, which is a desirable outcome for theoretical estimation of polyphenol release. Several researchers have highlighted that theoretical migration models that overestimate the release of antioxidants into food are useful for the preliminary design of active food packaging to avoid exceeding the allowable antioxidant concentration limit for food (Gavriil et al., 2018; Stärker & Welle, 2019). Underestimation of the polyphenol release by the models may result in the development of packaging material that releases antioxidants into food in concentrations higher than the allowable limit (Gavriil et al., 2018; Stärker & Welle, 2019). The exposure of consumers to antioxidants higher than the allowable limit (60 mg/kg of food) can be a health hazard (Beigmohammadi et al., 2016; EU, 2011; Peighambardoust, Beigmohammadi, & Peighambardoust, 2016). Gavriil et al. (2018) highlighted that migration models should only be utilised for active packaging material design when the model predictions deviate less than 70 % from the experimental results. In this study, the least deviation of the Migratest predictions from experimental results was recorded for the fatty food simulant (< 66.4 %) when compared to the other simulants. More importantly, the deviation of the models was less than 70 %, providing a basis for using migration models for designing AH-ACNC based active packaging material for fatty food packaging. Notably, a logarithmic trend best describes (average R^2 of 0.87, Table S4) the experimental polyphenol release pattern over the release duration (Fig. 4).

3.4.3. Antioxidant activity of the food simulants as affected by polyphenol release by the acetylated hemicellulose-based films

The antioxidant activity of the food simulants was dependent on temperature, time and type of simulant. The antioxidant activity increased with an increase in temperature from 5 °C to 40 °C in all the food simulants investigated (Fig. 5). This observed phenomenon is crucial as free radicals that promote food spoilage tend to increase, especially for food stored at 5 °C, as temperature increases to 40 °C. Therefore, an increase in the antioxidant activity of the food, as temperature increases, minimises the quantity of free radicals in food, thereby, reducing food spoilage (Malhotra, Keshwani, & Kharkwal, 2015). The food simulant that had the highest antioxidant activity was the fatty food simulant at 40 °C. This could be because the highest release of polyphenols by the films was into the fatty food simulant (Fig. 5) when compared to the other simulants. On the other hand, the antioxidant activity of the alcoholic, aqueous and acidic food simulants increased until a certain time and then decreased. The decline in the antioxidant activity of these simulants could suggest that there was interference on the antioxidant capabilities of the polyphenols in the simulant by co-migrated film material (Fig. 2a) (Ribeiro, Barbosa, Queiroz, Knödler, & Schieber, 2008). The antioxidant profiles (Fig. 5) were similar to those of the polyphenol release (Fig. 4). by the AH-ACNC/PCL films, implying that there was a correlation between the polyphenol content of the simulant and antioxidant activity. Conclusion

AH-based films hydrophilicity and solubility in food simulants can be minimised by reinforcing the AH films with 50 % ACNC of high DS (2.34) and coating the AH-ACNC films with PCL. The AH-based films were least soluble in the fatty food simulant when compared to the other food simulants, suggesting that their application should be for non-water-based systems and for storage in dry places. AH-ACNC-PCL films were able to encapsulate and release mango polyphenols into

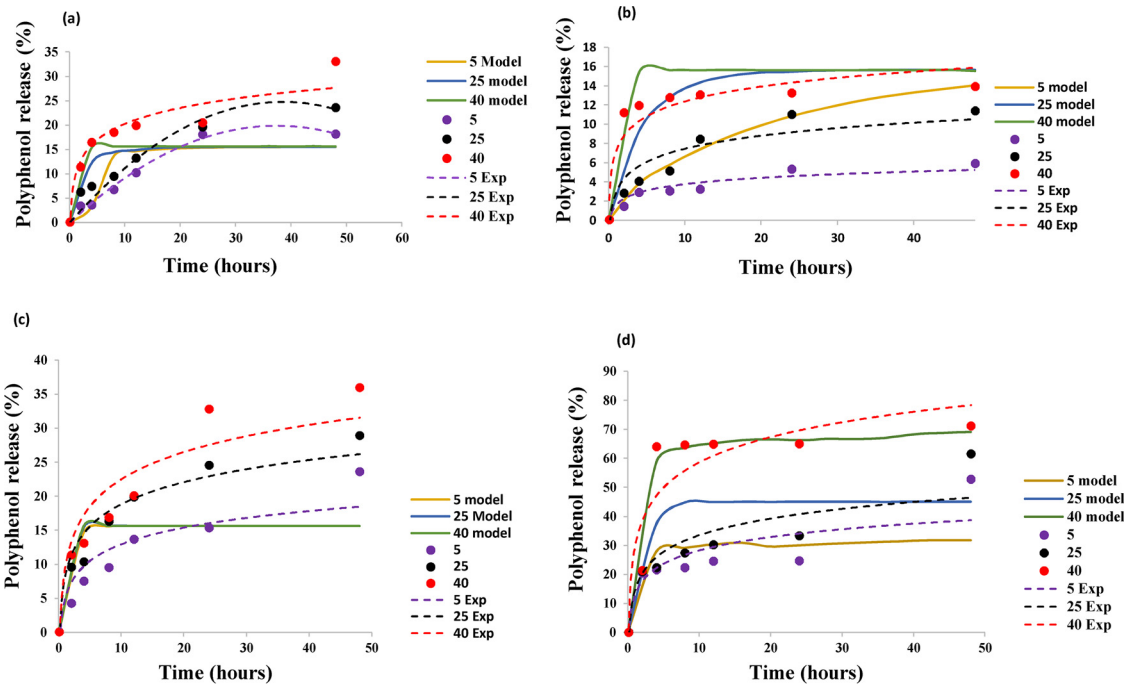

Fig. 4. Effect of temperature and time on polyphenol release by the acetylated hemicellulose-based active packaging into the (a) aqueous, (b) acidic (c) alcoholic and (d) fatty food simulant. 5, 25, and 40 represent temperatures, in degrees Celsius, at which the experiments and modelling were done. The dots in the figure are the experimental results, the dashed lines are the fitted polynomial curves to the experimental data and the solid lines are the model predictions. Exp represents experimental results.

simulants in response to temperature and time. However, integrating polyphenols into the AH-ACNC/PCL films, compromised some of the mechanical and functional properties of the films such as tensile strength and moisture barrier capabilities respectively. Ficks' migration models are best suitable for predicting release of polyphenols, encapsulated in the AH films, into the fatty food simulant. Minimal dissolution of AH-ACNC films in the fatty simulant coupled with the ability to release polyphenols with detectable antioxidant activity into the fatty simulant, indicates that the films have potential application as active food packaging material for fatty foods. In addition, the film release of the bioactive substances into the fatty simulant can be modelled at design stage which can contribute towards cost effective design of packaging material.

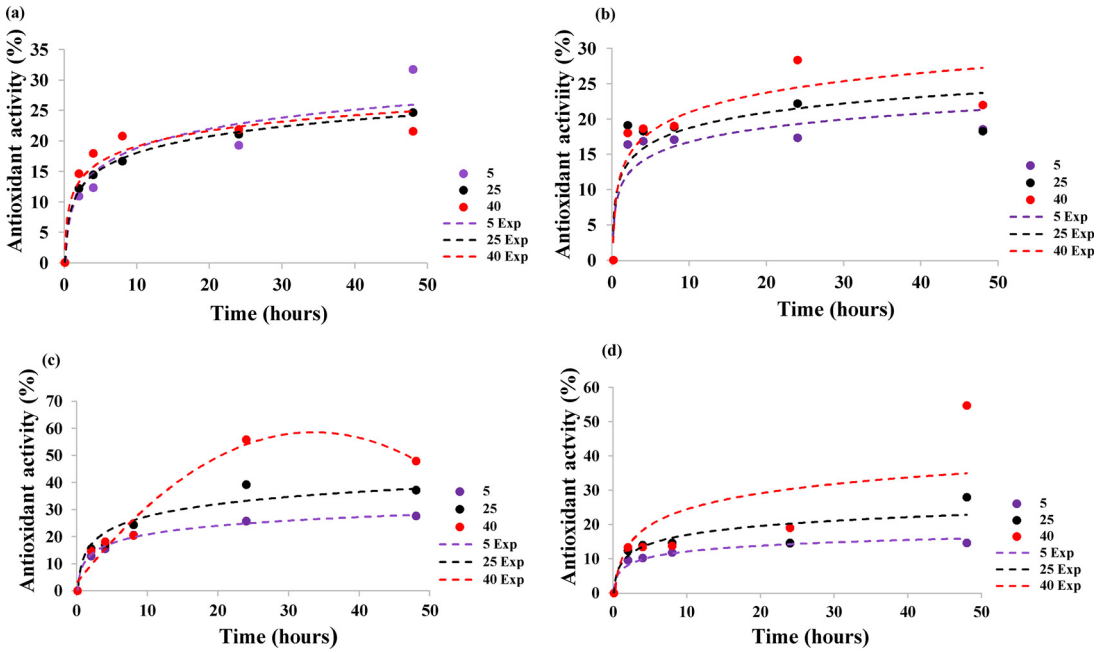

Fig. 5. Antioxidant activity of the (a) aqueous, (b) acidic (c) alcoholic and (d) fatty food simulant in contact with acetylated hemicellulose-based active packaging as affected by temperature and time. 5, 25, and 40 represent temperature, in degrees Celsius, at which the experiments and modelling were done. The dots in the figure are the experimental results, the dashed lines are the fitted polynomial curves to the experimental data. Exp represents experimental results.

CRediT authorship contribution statement

Lindleen. R. Mugwagwa: Conceptualization, Investigation, Methodology, Writing - review & editing, Validation, Formal analysis, Funding acquisition. **Annie F.A. Chimphango:** Supervision, Resources, Conceptualization, Writing - review & editing, Funding acquisition.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.fpsl.2020.100481.

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