ORIGINAL PAPER

Design, synthesis and antimicrobial properties of cellulose-based amine film

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Abstract
Film directing toward applications in food packaging and counter top coating with ability of inhibiting antimicrobial growth is important for maintaining food freshness and reducing bacteria transmittance. In this work, cellulose-based fatty amine with antimicrobial functionality covalently attached to cellulose backbone was synthesized. The synthesis was performed in a three-step process that involves cellulose oxidation, amination of oxidized cellulose using fatty amine and reduction. Films composites with various proportions of cellulose-based amine and cellulose triacetate were prepared. The films morphologies, tensile strengths, percent of elongation and contact angle were evaluated. The cellulose-based amine showed excellent antimicrobial activity against gram positive and moderate activity toward gram-negative bacteria. The films prevented the growth of gram-positive bacteria by 99.99%. Results indicate a good mechanical properties and bioactivities of produced film which makes it suitable for use in food wrapping application.

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Introduction

Natural product-based films with antimicrobial properties are becoming an attractive area of research for academic and industries. Particularly those directing toward commercial applications such as packaging and counter top coating received the most attention. Films with antimicrobial properties are an exceptional way of inhibiting bacteria growth on the food surface while maintaining food freshness and safety [1, 2]. Antimicrobial films can also be used as a coating material for the inside surface of containers designed for liquid food such soup and beverage [3, 4]. Wrapping the food containers with antimicrobial films could also help in reducing the amount of preservatives added to the food, thus maintaining original food flavor [4–6].

The present technology of making films with antimicrobial properties involves physical attachment of the antimicrobial reagents to the film surface by certain processes such as coating [7]. In another recent approach, composite films with immobilized nanoparticles antimicrobial activities were prepared, and some of these composites showed excellent antimicrobial activities [8, 9].

One major issue with the physical attachment approach is a large amount of antimicrobial agents or preservatives to migrate from the film surface to the food structure thus affecting food flavor and freshness. For this reason, methods other than physical attachment technique could be more effective in this matter [3, 4].

In the packaging area, mainly synthetic films are used, due to their high tensile strength, low permeability and low cost [10]. One major disadvantage in the synthetic film is the biodegradability, and the non-biodegradability will contribute to the environmental disposal issue. This issue steered the interest in natural-based films [10]. The alternative film is expected to be a new horizon for creating new markets for natural products and contributes to solving environmental pollution. One solution is the use of biodegradable film made from polysaccharides such as cellulose.

The use of natural products such as cellulose for making films is restricted by several drawbacks, like their hydrophilicity which cause the natural-based films to have high permeability to water vapor [11–13].

So far, chitosan is the main component of the natural product-based film with antimicrobial properties [14]. One major disadvantage of the natural-based reagent used for this purpose is they have limited antimicrobial efficiency. The antimicrobial efficacy of chitosan films was boosted by incorporation of natural antimicrobial agents like essential oils [15] such as those extracted from cinnamon, clove, fennel, garlic, ginger, or thyme. Ginger (*Zingiber officinale*) is another example of a natural product with antimicrobial activity [16]. A recent study showed that the edible film made from chitosan enriched with green tea extracts has potential to reduce both foodborne viruses and bacteria [5].

The main issue with the essential oils is they have hydrophobic properties, so they are not very compatible with chitosan, a legitimate reason to make them migrate from the film to the wrapped food [15, 17]. Also, the essential oil must be added to the film at high concentration to achieve reasonable efficacy. High

add-on of essential oil may cause adverse effect on food flavors and odors as mentioned above, affect the physical properties of the film and raise the film production cost [18, 19].

One approach to an effective antimicrobial film free of the previously mentioned disadvantage is a film that has an antimicrobial agent covalently bonded to the film structure. In this work, a cellulose-based film with alkyl amine functionality that is covalently bonded to cellulose structure was developed. The film was made from attaching a fatty alkylamine to the cellulose backbone. The fatty amine affords two advantages, and it acts as plasticizer and added antimicrobial properties to the film. The film has high transparency and good tensile strength and showed excellent antimicrobial activity.

Experimental

Materials and methods

All chemicals used in this work were purchased from Aldrich Chemical Company and used without any further purification unless otherwise specified.

The following instruments were needed to accomplish this research:

^{1}H NMR spectra were recorded on 263 GHz Klystron 400 MHz instrument (Brucker) with $(CD_3)_2SO$ as solvent and $(CH_3)_4Si$ as internal standards. All ^{1}H-NMR experiments are reported in δ units.

The FT-IR spectra were recorded on a Nicolet spectrometer (6700 FT-IR, Thermo Fisher Scientific, Waltham, USA). The film morphology was examined using scanning electron microscopy (SEM, S-4800; Hitachi, Tokyo, Japan) at an acceleration voltage equal to 3.0 kV. The analyzed samples were coated with gold using Cressington Sputter Coater (Ted Pella, Inc., Redding, CA, USA). The standard thermogravimetric analysis was carried out using the TGA Q500 and Q50 TA instrument (Newcastle, USA) at a temperature range from 20–900 °C and a heating rate of 10 °C/min.

The contact angle was measured using Cahn DCA 322 (Thermo Cahn, Madison, WI, USA)). The measurement was carried out by placing a drop of distilled water (10 μL) using a micropipette on the film surface, the experiment was repeated in triplicate, and the contact angle was determined using instrument software.

Cellulose amine polymer

Oxidation of cellulose to 2, 3-dialdehyde cellulose (CAD-1)

The cellulose used in this work was isolated from olive industry solid waste according to a procedure developed at our laboratory [20, 21]. A sample of the obtained cellulose (20.0 g, 123.5 mmol/anhydroglucose unit) was place in an Erlenmeyer flask (1.0 L) and suspended in a 0.5 L deionized water. The flask was wrapped with aluminum foil, and then, sodium periodate ($NaIO_4$, 32.1 g, MM = 213.9 g/mol,

0.15 mol) was added to the suspension in one portion. The reaction mixture was placed in a heating mantel and heated at 45 °C while being mixed with a mechanical mean for about 8 h. Produced cellulose aldehyde was collected by suction filtration and washed with a plenty of water (3×500 mL). Cellulose content of aldehyde functionality was determined to be about 1.81/AGU following a published procedure [22, 23]

Aldehyde per repeat unit of cellulose

A sample of an oxidized cellulose (1.00 g) was suspended in a 50.0 ml of 2-propanol. The suspension was stirred for 10 min, and then, 10.0 ml of distilled water was added to it. The pH of the mixture was adjusted to 3.50 using 5.0% HCl. The pH of aqueous solution of hydroxylamine hydrochloride (5.0% by weight) was adjusted to 3.5 using 5.0 wt% HCl solution. The hydroxylamine hydrochloride solution was added to the oxidized cellulose suspension and stirred for 6.0 h and then titrated with a 0.5 N NaOH solution to a pH of 3.5 end point.

The aldehyde content was then calculated using the following equation:

$$[Ald] = V_{NaOH} . N_{NaOH} * 162g/\text{anhydroglucose repeat unit}/W_{OC}$$

[Ald]: is the aldehyde content in mmol per anhydroglucose repeat unit, V_{NaOH} is the volume of NaOH (mL) used in the titration, N is the normality of the NaOH (eq/L), and W_{OC} is the dry weight of oxidized cellulose (g) used in titration.

Cellulose dodecyl amine (CDDA-3)

Oxidized cellulose (10.0 g, 61.0 mmol of AGU) and dodecyl amine (10.0 g, 54.1 mmol) were suspended in methanol (100 mL) in a round bottom flask. The reaction mixture was heated at 70 °C for 12 h. During this period of reaction, cellulose imine was produced. Sodium borohydride (3.0 g, 81.0 mmol) was added to the reaction and stirred for 6.0 h at room temperature. Excess sodium borohydride was destroyed by the addition of ammonium chloride solution (0.5%). The pH of the suspension was measured to be about 4.6. The prepared cellulose amine polymer was collected by suction filtration, washed with distilled water and ethyl alcohol and air-dried.

N-Methyl Dodecyl Amine (N-MCDDA-5)

Oxidized cellulose (10.0 g, 61.0 mmol of AGU) and N-methyl decylamine (10.8 g, 54.1 mmol) were suspended in methanol (100 mL) in a round bottom flask. The reaction mixture was heated at 70 °C for 12 h, and during this period of reaction, cellulose iminium salt was produced. The reaction mixture was then treated with sodium triacetoxyborohydride (17.2 g, 81 mmol) prepared in situ according to a published procedure. The reaction was stirred at room temperature for 8.0 h. A solution of ammonium chloride (0.5 wt.%) was added to the reaction mixture to eliminate excess sodium triacetoxyborohydride. The pH of the suspension was measured to be about 4.8. The

produced cellulose polymer with an ammonium functionality was collected by suction filtration, washed with distilled water and ethyl alcohol and air-dried.

Preparation of cellulose acetate

The preparation of cellulose acetate was carried out in a Pyrex reaction kettle (0.5 L). The reaction kettle was equipped with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, gas inlet polyethylene tubing inserted through an adapter fitted with a rubber septum and a gas outlet adapter connected to a gas trap partially filled with oil. To the reaction kettle was added cellulose powder 50 g (300 mmol/anhydroglucose repeat unit), followed by 100.0 mL acetic acid and 1.0 mL concentrated sulfuric acid. The reaction was stirred at room temperature under N_2 for about 20 min, then excess acetic anhydride (1.2 mol, 122.0 g, 133.0 mL) was added. The mixture was stirred at room temperature until a clear thick gel was obtained (90 min). The reaction mixture was poured into water (0.5 L), stirred for 15 min and then filtered. The collected solid was suspended in a 5% solution of sodium bicarbonate, filtered, washed with water and dried. Then, it was ground in a Wiley mill to pass through a 20-mesh screen. ^{1}H-NMR of cellulose acetate (DMSO) δ (ppm): 1.95 (Me-2), 2.03 (Me-3), 2.14 (Me-6), 3.67 (H5), 3.83 (H4), 3.97 (H6′), 4.38 (H6), 4.55 (H1), 4.79 (H2), 5.17 (H3).

Antimicrobial activity

The antimicrobial tests were performed by Biosan Laboratories, Inc. in. Warren, MI.

The test was carried out as follows: The tested films were cut into circles with a diameter of 5.0 (±0.1) cm. Circles samples were placed in sterile empty specimen cups and inoculated with a 1.0 ml suspension of test organism, allowing the inoculum to completely cover the sample surface. Each sample was incubated for a specific contact time (2 h), then transferred to a 10 mL of neutralizing solution and vigorously shaken by vortex. The resulting suspension was inoculated to media supportive of bacterial growth and incubated at 36 ± 2 °C for 18–24 h. The colonies 0 were counted. At each designated time point, the process was repeated twice. The test was performed on three organisms: Pseudomonas aeruginosa, Staphylococcus aureus and *Escherichia coli (E. coli)*. The percent reduction in bacteria number was calculated according to the equation below.

$$\%\text{Reduction} = \frac{\text{Control } (cfn/mL@T = 0) - (\text{Sample } cfn/mL@T = \text{time point})}{\text{Control } (cfn/mL@T = 0)} \times 100$$

Results and discussion

Cellulose in powder form used in this study was extracted from olive industry solid waste locally known as Jeft, and it was extracted using a modified version of the Kraft pulping process and then was whitened using a multi-step bleaching process

[20, 21]. The isolated cellulose in powder form was converted to cellulose alde-hyde by oxidation with sodium periodate [24]. The aldehyde content was about 1.81 per anhydroglucose repeat unit as was determined according to a reported titration method [23, 24].

The FT-IR spectrum of the prepared cellulose dialdehyde (CAD-1) showed peaks at 1730 cm^{-1}, 1373 and 1142 cm^{-1}, assigned to carbonyl of aldehyde, C-O (stretch-ing) of alcohol and ether and C–O–C (stretching) of β-glycosidic linkage, respec-tively. The carbonyl band (1730 cm^{-1}) showed as a weak peak could be due to the hydration and acetal formation [25, 26].

Preparation of cellulose dodecylamine (CDDA-3)

The aldehyde is a versatile functional group, and it can be converted to a variety of functional groups such as carboxylic acid, primary alcohol and amine. It undergoes a nucleophilic addition reaction with amine to form imine which can be reduced to an amine using sodium borohydride. The reaction of CAD-1 with dodecyl amine is shown in Scheme 1.

The reduction of cellulose imine intermediate was performed in methanol using sodium borohydride (Scheme 1). Excess sodium borohydride was destroyed by the addition of ammonium chloride, and during this process, amine protonation and the formation ammonium functionality could occur. Ammonium compounds are known to have antimicrobial activities. The pH of the ammonium suspension was deter-mined to be about 4.6.

During the synthesis of CDDA-3, a sample from the reaction mixture was with-drawn before the addition of the reducing agent. The withdrawn sample was centri-fuged, and the precipitate (solid) was washed with methanol, dried and analyzed by FT-IR. This step was carried out to confirm the cellulose imine (CDDI-2) formation. The FT-IR spectrum (Fig. 1) for cellulose dodecyl imine shows a peak at 1650 cm^{-1}, and it corresponds to the imine group (C=N). The weak broad peak at 1610 could be attributed to water that associated with cellulose. The two bands at 2922 and 2851 cm^{-1} are corresponding to the symmetric and asymmetric stretching vibration of the C–H of the aliphatic chain of the amine. The broad band at about 3354 cm^{-1} is a combination of multi-peaks originated from OH and NH stretching vibrations of secondary amines. The presence of strong peaks at 2922 and 2851 cm^{-1} is an indi-cation of the fatty group attachment onto the cellulose backbone. The strong peak at 1050 cm^{-1} corresponds to C–O and C–O–C stretching.

The FT-IR spectra of cellulose dodecylamine **(CDDA-3)** are shown in Fig. 2. It shows similar peaks to those present in the IR spectrum of cellulose dodecyl imine with the disappearance of the peak at 1650 cm^{-1} corresponding to imine (C=N) bond and the appearance of N–H 3345 cm^{-1}.

Preparation of cellulose *N*-methyl dodecylamine (*N*-MCDDA-5)

Cellulose aldehyde was also reacted with *N*-methyl dodecylamine (Scheme 2), as in the preparation of the previous amine (CDDA-3), it was converted to cellulose imine
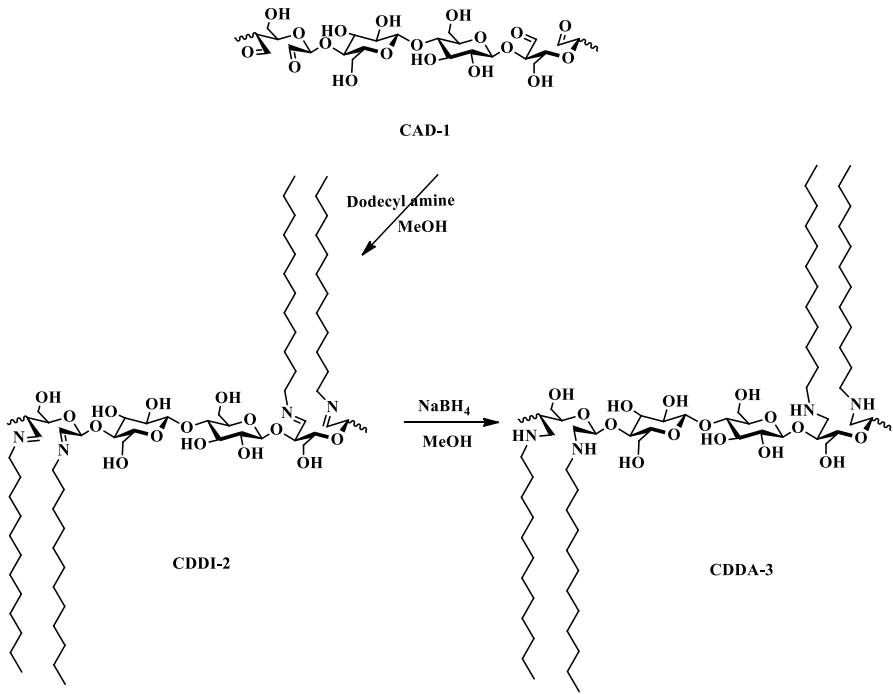
Scheme 1 Conversion of cellulose dialdehyde to cellulose amine (CDDA-3)
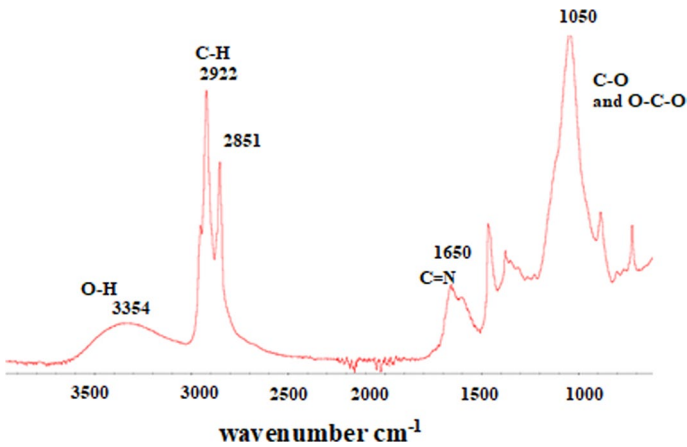

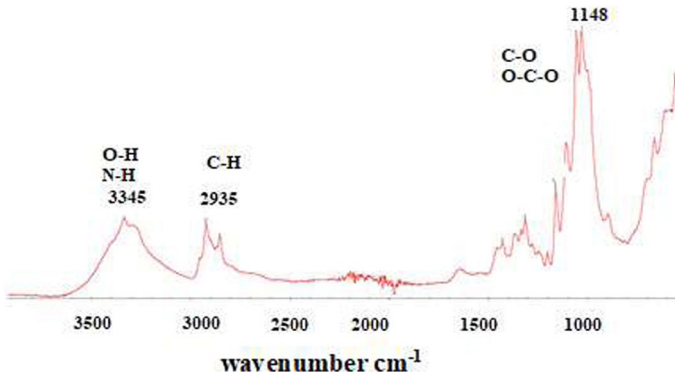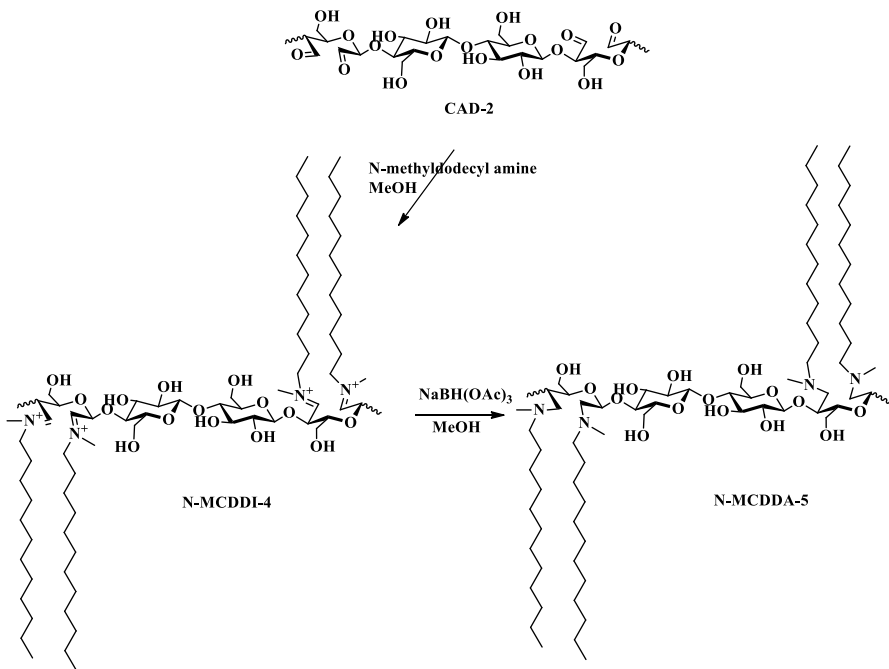**Fig. 1** FT-IR of cellulose dodecylamine (CDDI-2)

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Fig. 2 FT-IR of *N*-MCDDA-3

Scheme 2 Reduction of cellulose imine to cellulose amine (*N*-MCDDA-5

and then reduced with triacetoxyborohydride to cellulose amine *N*-MCDDA-4, and triacetoxyborohydride was prepared according to a published procedure [27].

FT-IR of cellulose *N*-methyldodecylamine (*N*-MCDDA-5)

The FT-IR spectra of cellulose amine polymer **5** are shown in Fig. 3. The spectrum shows a weak broad band at 1650 cm^{-1} which could be related to residual (C=N)
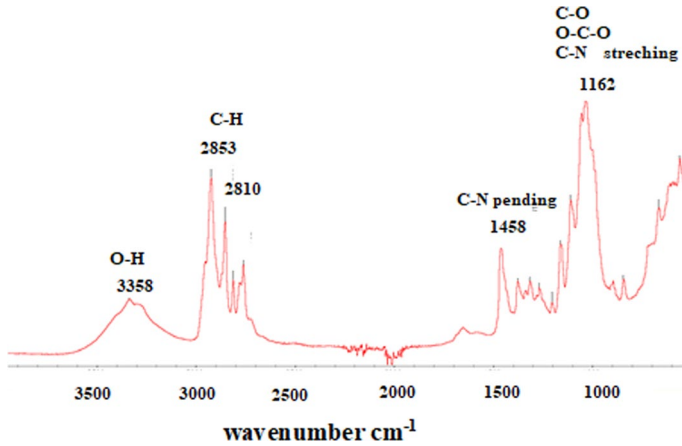
Fig. 3 FT-IR of cellulose *N*-methyl dodecylamine

iminium salt. The two peaks at 2810 and 2853 cm^{-1} are corresponding to the symmetric and asymmetric stretching of the C-H bond of *N*-methyl amine and aliphatic chain of the amine. The broad adsorption peak at about 3358 cm^{-1} corresponds to the O–H stretching vibrations.

Cellulose acetate

Cellulose acetate used in this work was prepared from reacting cellulose isolated from olive industry solid waste [20, 21] with acetic anhydride in acetic acid using a catalytic amount of concentrated sulfuric acid. The ^{1}H NMR spectra of prepared cellulose acetate are shown in Fig. 4. The peak integration showed that the degree of
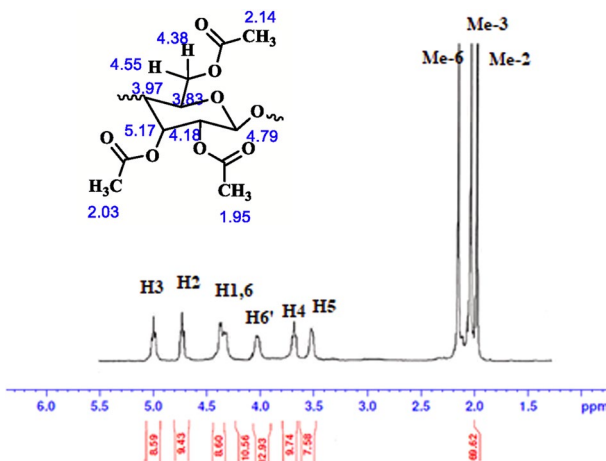
Fig. 4 Proton NMR of cellulose acetate

substitution is about 2.67 of acetyl groups per anhydroglucose repeat units. Chemical shifts of the cellulose acetate protons and the methyl protons are consistent with those published in the literature [28].

Film formation and properties

Film casting was carried out by dissolving a known amount of cellulose amine in dichloromethane, and the produced solution was transferred to an evaporating plate and covered with a beaker and left for slow evaporation in the fume hood. A smooth regular film was obtained, and the image of the obtained film from casting 0.5 g of CDDA-3 is shown in Fig. 5a.

Film transparency and strength were enhanced by adding cellulose triacetate. In this case, a solution of methanol and dichloromethane (1:2 ratio by weight) was used as dissolution solvent.

Film morphology

The morphology of the film composites 2 (Table 2) and 5 (Table 3) was subjected to analysis by SEM. The obtained images are shown in Fig. 6, and the images show a smooth and homogeneous surface with no phase separation and excellent packing, which indicate the compatibility between cellulose amine and cellulose acetate.

Contact angle

The contact angles of the CDDA-3, *N*-MCDDA-5 and cellulose acetate were determined, and the collected results are shown in Table 1. As shown in Table 1, the high contact angle reflects the hydrophobicity of the film. Films made from CDDA-3 and *N*-MCDDA-5 showed much higher contact angle than that for cellulose acetate. The higher contact angle is an indication of the material hydrophobicity which could be attributed to the presence of the long hydrocarbon chain attached to cellulose backbone. As shown in Table 1, the contact angles of cellulose acetate and cellulose amines make them compatible in regard to making a homogenous film.

Films physical and mechanical properties

Tensile testing was performed on a Instron 5965 series (MA, USA) instrument fitted with a 200 N load cell with speed of 1.0 mm/min, and the initial distance between the grips was 30 mm. Five specimens of each film were tested at room temperature, and the average values are reported in Tables 2 and 3. The composites showed tensile strength comparable to that of cellulose acetate. The elongation was improved compared to cellulose acetate, an indication that the fatty amine chain behaved as a plasticizer for cellulose acetate.

Films made from pure cellulose amines were little clumpy (Fig. 5a), and their tensile strength values were low. For this reason, the tensile strength values were not reported.
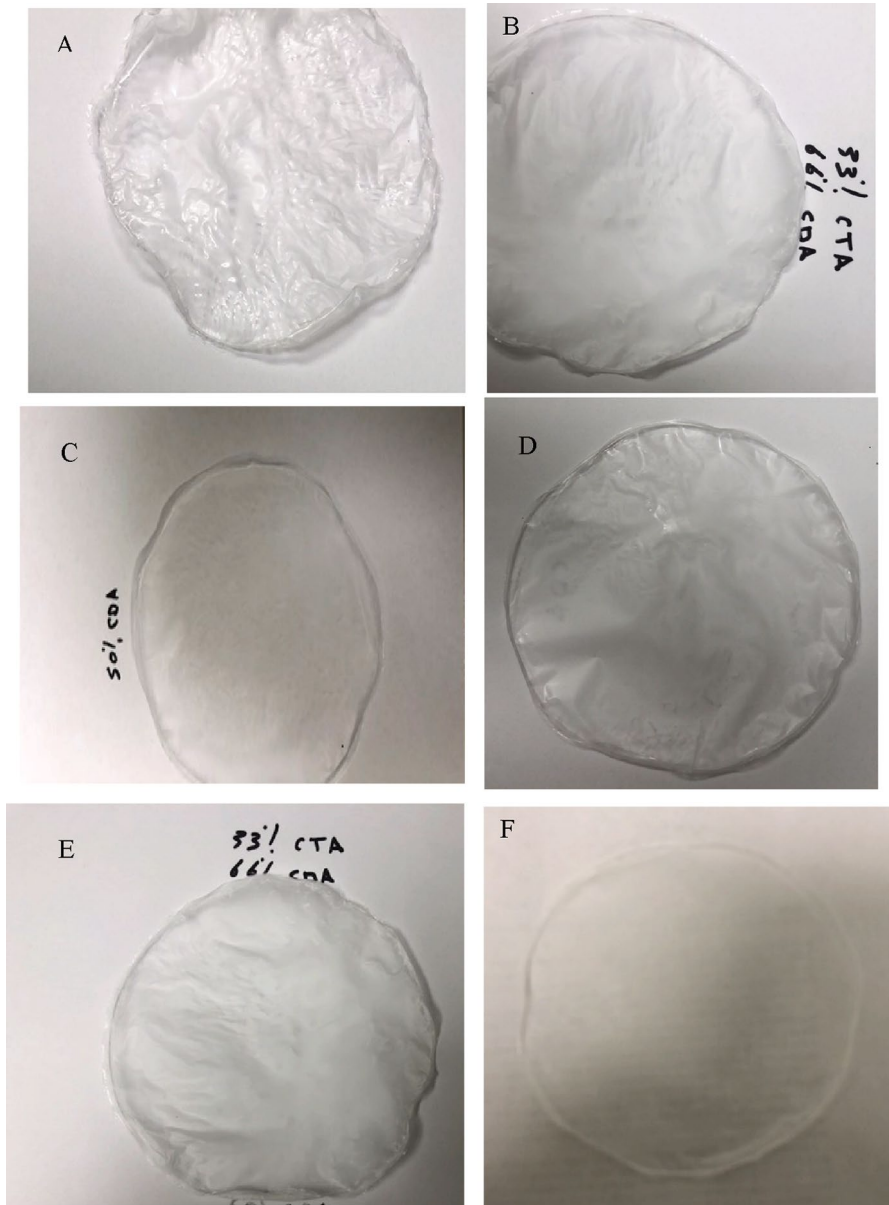
Fig. 5 **a** CDDA-3 film. **b** CDDA-3 and CTA in 3:1 ratio by weight. **c** CDDA-3 and CTA in 1:1 ratio by weight. **d** CDDA-3 and CTA in 1:3 ratio by weight. **e** N-MCDDA-5 and CTA in 3:1 ratio by weight. **f** N-MCDDA-5 and CTA in 1:1 ratio by weight
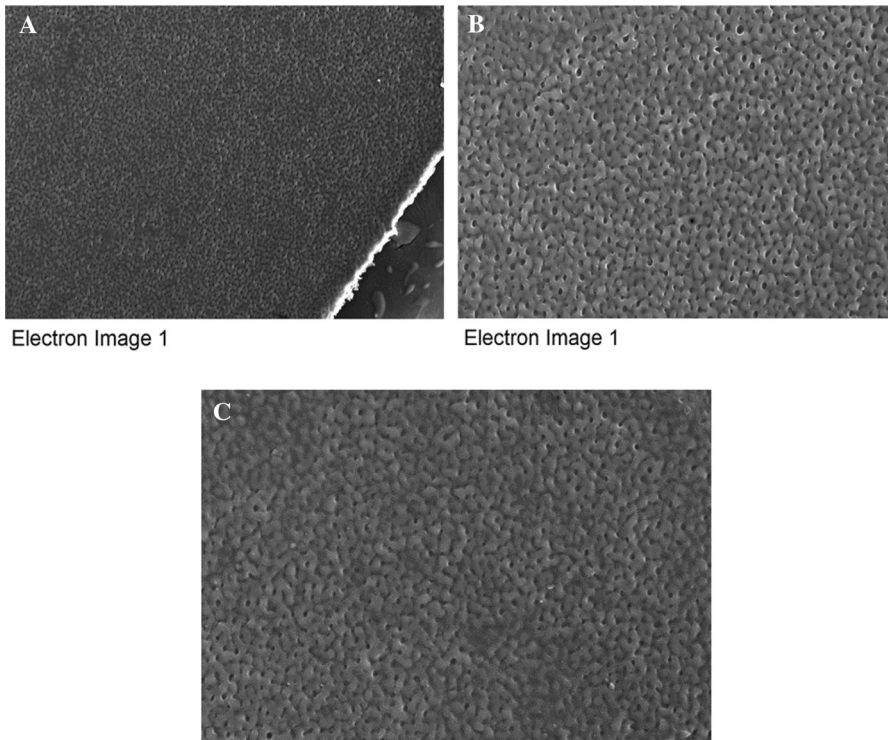
Fig. 6 SEM image of films made from a mixture of **a** CDDA-3 and cellulose triacetate in 2:1 ratio by weight (film 2, Table 2) at magnification of 40x; **b** 60x; and **c** *N*-MCDDA-5 and cellulose triacetate in 2:1 ratio (film 5, Table3) at magnification of 60x

Table 1 Water contact angle values of cellulose films

Sample	Contact angle
Cellulose acetate	66.8
CDDA-3	98.5
N-MCDDA-5	103.2

Table 2 Physical and mechanical properties of CDDA-3/CTA film

Film composite no	Components weight ratio (wt%)		Tensile strength (MPa)	Elongation (%)	Tg (°C)
	CDDA	CTA			
1	66	33	62 ± 8	7 ± 2	108.2
2	50	50	67 ± 8	7 ± 2	135.0
3	33	66	73 ± 8	5 ± 2	148.2
4	–	100	86 ± 8	4 ± 1	189

Table 3 Physical and mechanical properties of *N*-CDMDA-5/CTA films

Film composite no	Components weight ratio (wt%)		Tensile strength (MPa)	Elongation (%)	Tg (°C)
	CNMDA	CTA			
5	66	33	59 ± 8	8 ± 3	107.5
6	50	50	66 ± 7	6 ± 3	133.2
7	33	66	71 ± 8	6 ± 2	145.6
4	–	100	86 ± 8	4 ± 1	189

Antimicrobial activities of CDA polymers

The antimicrobial activities of the two cellulose diamine composites 2 (Table 2) and 6 (Table 3) were evaluated against three types of bacteria: two gram negative and one gram positive. Both polymers showed excellent activities against gram negative and medium activity against the gram-positive bacteria. The results are summarized in Table 4. A second sets of films with pH value of 6.5 were also evaluated against the bacteria shown in Table 4, and change on the activities was observed.

Conclusion

This work presents an innovative antimicrobial film suitable for application in food warping and countertop coating. The film was prepared from cellulose extracted from the waste of olive industry. The extracted cellulose was oxidized to cellulose aldehyde and then reacted with fatty amine to produce cellulose imine. The cellulose imine was converted to cellulose amine by reduction with sodium borohydride. Two fatty imines were used for making cellulose-based amine dodecylamine and

Table 4 Percent reduction of three microbial cells by cellulose amine films

Cellulose amine composites	Bacterial cell	Reduction after 24 h vs control (%)
Cellulose and cellulose acetate	*Staphylococcus aureus*	0.0
	Klebsiella pneumonia	0.0
	E.coli	0.0
Film 2	*Staphylococcus aureus*	62.31%
	Klebsiella pneumonia	>99.00
	E.coli	>99.00
Film 6	*Staphylococcus aureus*	61.53%
	Klebsiella pneumonia	>99.00
	E.coli	>99.00

N-methyldodecylamine. The structures of the prepared cellulose amines were confirmed by FT-IR. Films with various compositions of cellulose amines were prepared. The films mechanical properties were evaluated, and the antimicrobial activity of the films was examined against three organisms: Pseudomonas aeruginosa, Staphylococcus aureus and *Escherichia coli (E.coli)*. The films showed excellent antimicrobial activity against gram positive and moderate activity toward gram-negative bacteria. The films prevented the growth of gram-positive bacteria by 99.99%.

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