



## Green synthesis of stretchable ethyl cellulose film plasticized with transesterified sunflower oil

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### ABSTRACT

Sustainability and environmental consciousness drive research toward biomaterials and green synthesis. Traditional plasticizers derived from non-renewable sources have raised concerns due to their adverse impact on the environment and human health. As a result, there is a growing interest in replacing these traditional plasticizers with inexpensive naturally derived alternatives. One such promising compound that has gained considerable attention is vegetable oil. In this study, we investigated the feasibility of using transesterified sunflower oil as a plasticizer for ethyl cellulose (EC), a widely used hydrophobic biopolymer. The transesterification reaction, accelerated by the catalyst NaOH, resulted in the formation of short chemical compounds that improved the plasticity of EC films. The mechanical studies demonstrated a remarkable elongation break of approximately 94 %, setting a new record for this type of film. The plasticization process was confirmed through rheological and XRD studies, revealing a notable reduction in the elastic chain and crystallinity of the EC structure. The proposed process advances the state of the art in ethyl cellulose plasticization and stands out for its simplicity, cost-effectiveness, and environment-friendly approach. The synthesized films offer exciting possibilities for use in various applications including food packaging, transdermal drug delivery systems, and stretchable electronics.

### 1. Introduction

Cellulose is widely recognized as the most abundant naturally occurring and renewable organic polymer (Çetin et al., 2009). Ethyl cellulose is one of the most significant cellulose derivatives, a linear, non-branched polysaccharide with 1–4 glycosidic links in which ethyl groups (CH<sub>3</sub>CH<sub>2</sub>-) are substituted for the hydroxyl end groups of cellulose at the 2, 3, or 6 carbons of anhydrous glucose units (Fig. 1) (Ahmadi et al., 2022). In addition to the hydrophobic and barrier-forming characteristics, it is biodegradable and edible, non-toxic, low cost, and resistant to chemicals, heat, and sunlight, making EC a promising biomaterial (Horvat et al., 2022; Seddiqi et al., 2021). Ethyl cellulose-based formulations such as oleogel, micro/nanoparticles, and films have proven its significant role in many fields including the biomedical field, drug delivery systems such as binders (Huang et al., 2006; G. M. Khan & Meidan, 2007), coating agent (Murtaza, 2012; Muschert et al., 2009), and film-forming agent (Gohel & Nagori, 2009) and also for the encapsulation of pharmaceuticals (Sogol & Ismaeil, 2011). Moreover, EC also found applications in electronic devices and sensors, cosmetics, and food packaging (Horvat et al., 2022; X. Li et al.,

2015) as adhesives, fillers, and additives. EC employment for edible electronics, in particular as substrate and binder in electrodes for triboelectric nanogenerators, supercapacitors (Lamanna et al., 2023), batteries (Ilic et al., 2023), and transistors (Sharova et al., 2023), is a good example of an application that exploits a large number of its features. However, even though EC has been demonstrated to have good film-forming capabilities, the strong intermolecular H-bond connections and hydrophobic interactions between the EC chains have a negative impact on some crucial properties (e.g. processability and mechanical properties) limiting its potential application in new unexplored fields (Bodmeier & Paeratakul, 1994). Consequently, research is pushing to find novel solutions able to improve EC features but, at the same time, to save all those peculiar qualities of EC (such as edibility, biocompatibility, biodegradability, etc.) through its potential to create supramolecular structures.

Usually, polymer plasticity has been improved by introducing non-volatile plasticizers, which are low-molecular-weight chemicals added to a material to improve its flexibility, workability, and stretchability (Godwin, 2017). Due to its small molecule size, the plasticizer can embed itself between the intermolecular spaces of polymer chains,

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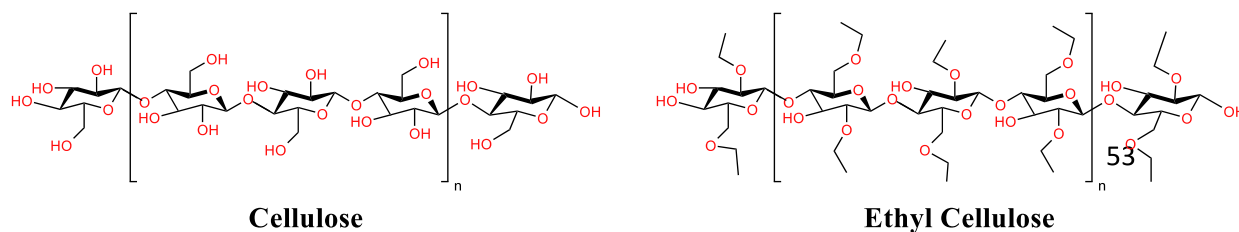


Fig. 1. Chemical structures of cellulose and ethyl cellulose.

Table 1

EC: Oil ratio for the preparation of ECSF films.

EC: SF oil ratio	EC N200	Sunflower oil
1:0	0.75 g	0 g
1:1	0.75 g	0.75 g
1:1.5	0.75 g	1.125 g
1:2	0.75 g	1.5 g

altering the polymer's three-dimensional structure and leading to a higher free volume within chains and improving molecular mobility (Wypych, 2004) by minimizing the secondary force and energy required for chain mobility (Doolittle, 1954, 1965; Kurtz et al., 1965). This way the plasticizers reduce macromolecule interactions improving properties such as chain flexibility, resistance to fracture, and dielectric constant while simultaneously lowering the tension of deformation, hardness, density, viscosity, etc. (Rosen, 1971). The plasticization also affects other physical properties like the degree of crystallinity, optical clarity and diffusion, and fire behaviour (Bialecka-Florjańczyk &

Florjańczyk, 2007; Galdeano et al., 2009). Effective plasticization involves strong molecular interactions and chemical compatibility, leading to a homogeneous and stable mixture of polymer and plasticizer which helps to avoid undesirable phenomena like migration, extractability, exudation, and volatility (Hammer, 1978).

The plasticizers used for modifying polymers are mostly derived from non-renewable sources and are usually used in either homogeneous or heterogeneous systems with non-green solvents (Hao et al., 2009). The most commonly used plasticizers are adipates, azelates, benzoates, phthalates, trimellitates, and phosphates, among them, derivatives of phthalates compose 87 % of the plasticizer industry (Haryono et al., 2017). Derivatives of phthalates such as dibutyl phthalate (DBP) and diethyl phthalate (DEP), dibutyl sebacate (DBS) were mainly used for the plasticization of EC (Frohoff-Hülsmann et al., 1999; He et al., 2006; Hyppölä et al., 1996; Tarvainen et al., 2003). Despite their merits, these present some technical and environmental drawbacks because of their volatility, toxicity, leachability, and processing instability. Due to their exposure-related harmful effects on human health, these plasticizers have drawn negative attention in recent years

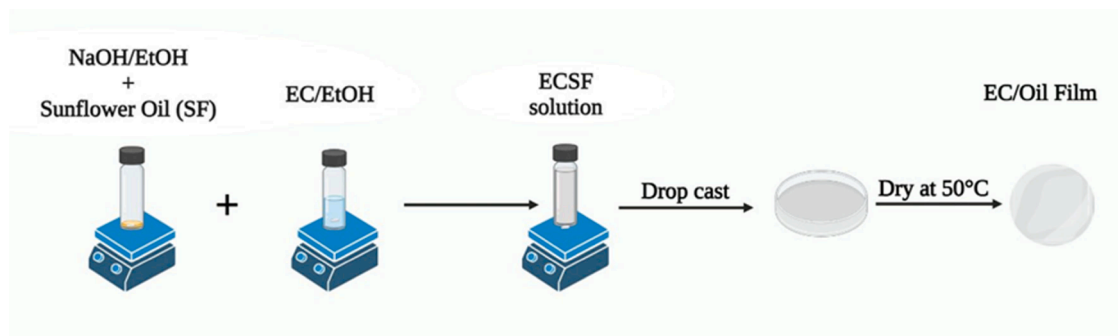
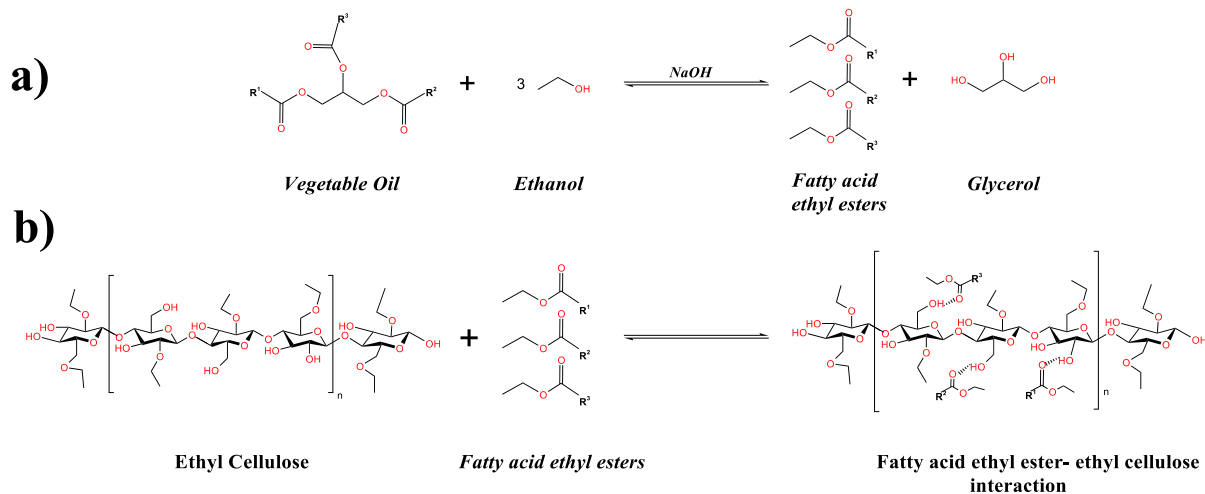
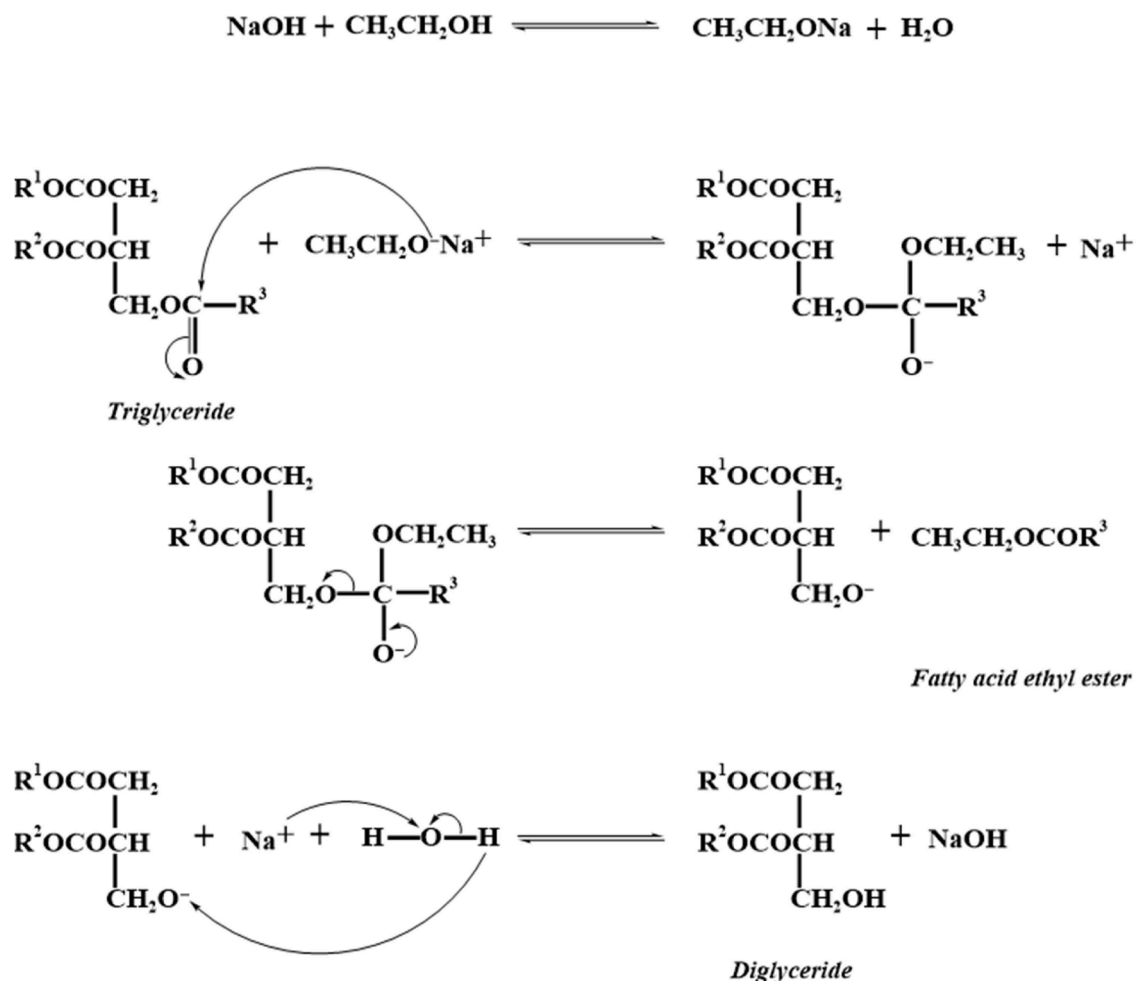


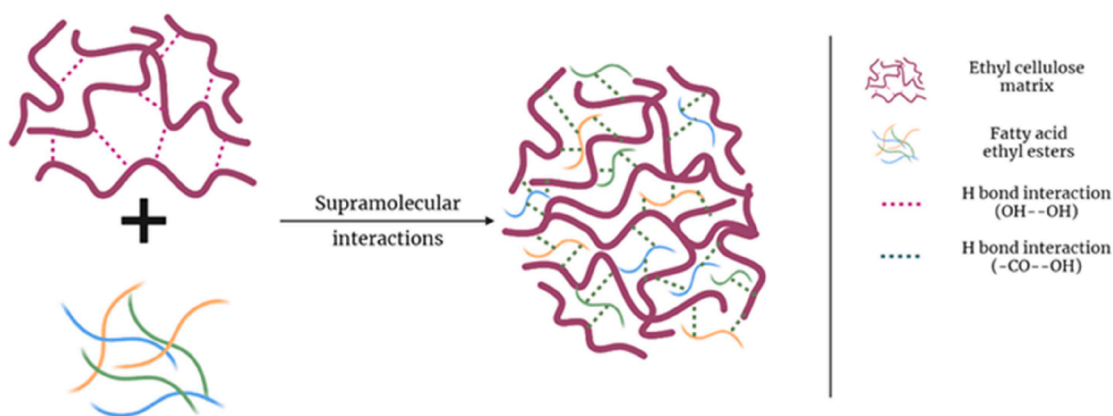
Fig. 2. The pictorial representation of the synthesis protocol of ECSF films.



Scheme 1. a) Transesterification reaction of sunflower oil and b) chemical illustration for the interaction of transesterification products with ethyl cellulose.



Scheme 2. Base catalysed mechanism of transesterification reaction.



Scheme 3. Supramolecular interaction between ethyl cellulose and fatty acid ethyl esters.

(Doelman et al. 1990; Haryono et al., 2017; Oie et al., 1997).

Consequently, studies are interested in obtaining green plasticizers that have low toxicity and performances comparable to synthetic ones in terms of plasticizing efficiency and low migration. An example of a green substitute for the current EC plasticizers is citrate derivatives like triethyl citrate (TEC) or other naturally derived plasticizers such as cardanol oil (Friuli et al., 2020). However, the EC films plasticized with TEC have exhibited poor performance on mechanical strength (Arthur H. Kibbe, 2000; Tarvainen et al., 2003). Other examples of EC films

additivated with green plasticizers include supramolecular composite films produced using biobased lipoic acid (Lin et al., 2021) and EC films modified with capsaicin as a plasticizer (Su et al., 2020). These studies demonstrate the potential of using natural compounds as plasticizers for EC and other polymers, highlighting the growing interest in sustainable and environment-friendly alternatives to traditional plasticizers derived from non-renewable sources.

Plasticizers derived from the epoxidation of vegetable oil are another studied solution. Vegetable oil (e.g., soybean oil, sunflower oil, peanut

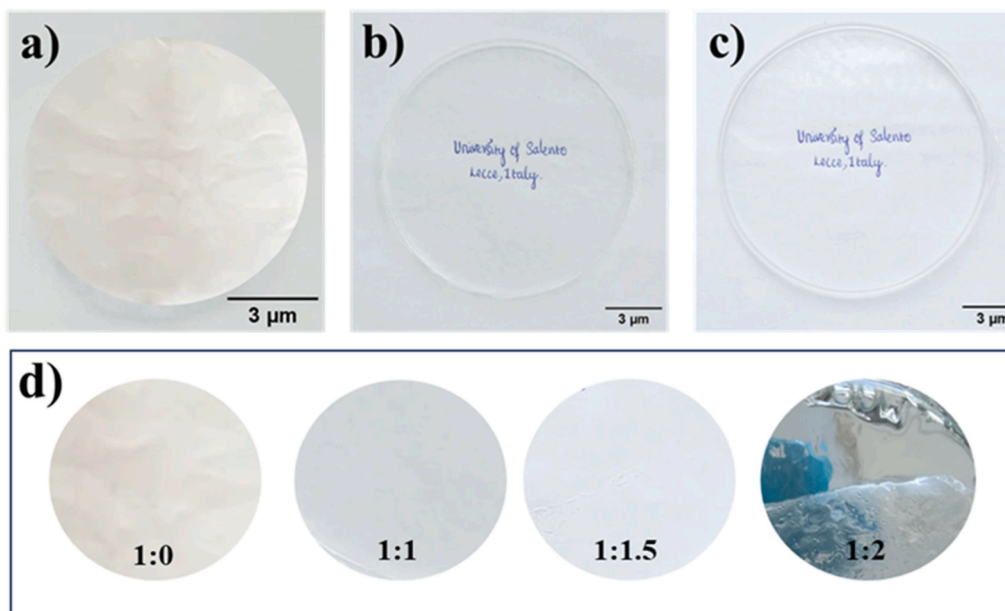


Fig. 3. Synthesized ECSF films a) 1:0 ratio, b) 1:1 ratio, c) 1:1.5 ratio and d) separation of oil from the film with increase of oil concentration.

oil, etc.) is an environment-friendly material, chemically a triglyceride consisting of three long fatty acid alkyl chains. They have been reported as substitutes for traditional plasticizers for the enhancement of flexibility of polymers like PVC, PLA etc. (Luo et al., 2020; Satapathy & Palanisamy, 2021; Volpe et al., 2018) and their plasticization effect was also investigated in EC films. However, the maximum deformation obtained for the EC films with 20 % of epoxidized soybean oil (ESO) used as a plasticizer was 13 % indicating poor performance (Yang et al., 2014). Dimeric acids synthesized from waste soybean oil have been investigated as an effective plasticizer for ethyl cellulose (Lee et al., 2015). In another study vegetable oil-based thioether polyol was used as a plasticizer for EC and achieved an elongation at break of about ~44 % (Yan et al., 2023). Polyols derived from ricinoleic acid and oleic acid were explored for the plasticization of EC and the maximum deformation obtained was about ~23 % for oleic acid-derived polyol containing one hydroxyl group (Lin, Li et al., 2021). Another strategy for using vegetable oils as plasticizers for EC is their direct incorporation into the polymeric network. However, the effectiveness of this approach is often limited by the presence of phase separation phenomena, which can restrict the amount of oil that can be added and thus limit the extent of plasticization achievable during film production.

We overtook these limitations and improved the effect of vegetable oil as a plasticizer by performing a transesterification reaction. In this study, we utilized NaOH, a strong base as a catalyst, to initiate the transesterification reaction of sunflower oil with ethanol (Otera, 1993; Schuchardt et al., 1998; Sivaprakasam & Saravanan, 2007). This transesterified sunflower oil was used to plasticize the ethyl cellulose polymer. The shorter non-volatile molecules resulting from the transesterification reaction of sunflower oil could function as an effective plasticizer for the ethyl cellulose films by generating a supramolecular system. This way is possible to improve the compatibility of vegetable oil and EC allowing a higher amount of oil as a plasticizer without phase separation and in this study, we successfully synthesized ethyl cellulose films plasticized with transesterified sunflower oil (ECSF films). The proposed process represents an innovative approach in the field of green plasticizers. Not only does it offer improved performance and versatility, but it also stands out for its simplicity, cost-effectiveness, and environment friendly nature. These factors make the proposed process a promising solution that aligns with the growing demand for sustainable and green practices in various industries.

## 2. Experimental section

### 2.1. Materials

Aqualon™ Ethylcellulose, EC N200 (48–49.5 % content of ethoxy group) was purchased from Ashland, Wilmington, United States. Sodium hydroxide pellets (NaOH)  $\geq 98$  %, and absolute ethanol (EtOH) 99.9 % were obtained from Sigma Aldrich, St. Louis, USA. Sunflower Oil was purchased from the local supermarket. All the above chemical reagents were used without any purification.

### 2.2. Methodology

#### 2.2.1. Synthesis of ECSF films

0.75 g of ethyl cellulose (EC N200) was dissolved in 25 g of absolute ethanol (EC/EtOH solution) and subjected to overnight stirring at 50 °C. In parallel, 0.8 % (w/v) of the catalyst solution was prepared by dissolving NaOH in absolute ethanol. 0.5 g of catalyst solution was mixed with sunflower oil with respect to each EC: Oil ratio (Table 1) in a vial and the solution was stirred at 400 rpm at 50 °C until the solution turned to a slightly yellow clear solution (Figure.S1). The previously prepared EC/EtOH solution was added to the Oil/NaOH solution and stirred overnight under the same reaction conditions. The homogeneous ECSF solution was then drop-cast into a glass petri dish (90 mm diameter) and kept in an oven to evaporate all the ethanol and water. The dry ECSF film was then cooled at room temperature and then subjected to various characterizations.

In addition to the ECSF films, we have synthesized ethyl cellulose films plasticized with sunflower oil (ECSF\* film) of the ratio 1:1.5 in the absence of catalyst NaOH to check the difference in stretchability with the same method. For the synthesis of ECSF\* film the sunflower oil was added directly to the previously prepared EC/EtOH solution and stirred overnight at 50 °C and at 400 rpm. Apart from the 1:1.5 ECSF films, we prepared 1:1.5 ethyl cellulose films plasticized with different transesterified vegetable oils such as soybean oil, and maize oil for determining their plasticization efficiency.

The synthesis of ECSF films at room temperature was affected by the coffee ring effect and non-transparency (Figure. S2). Thus, all the films were produced at 50 °C in the oven.

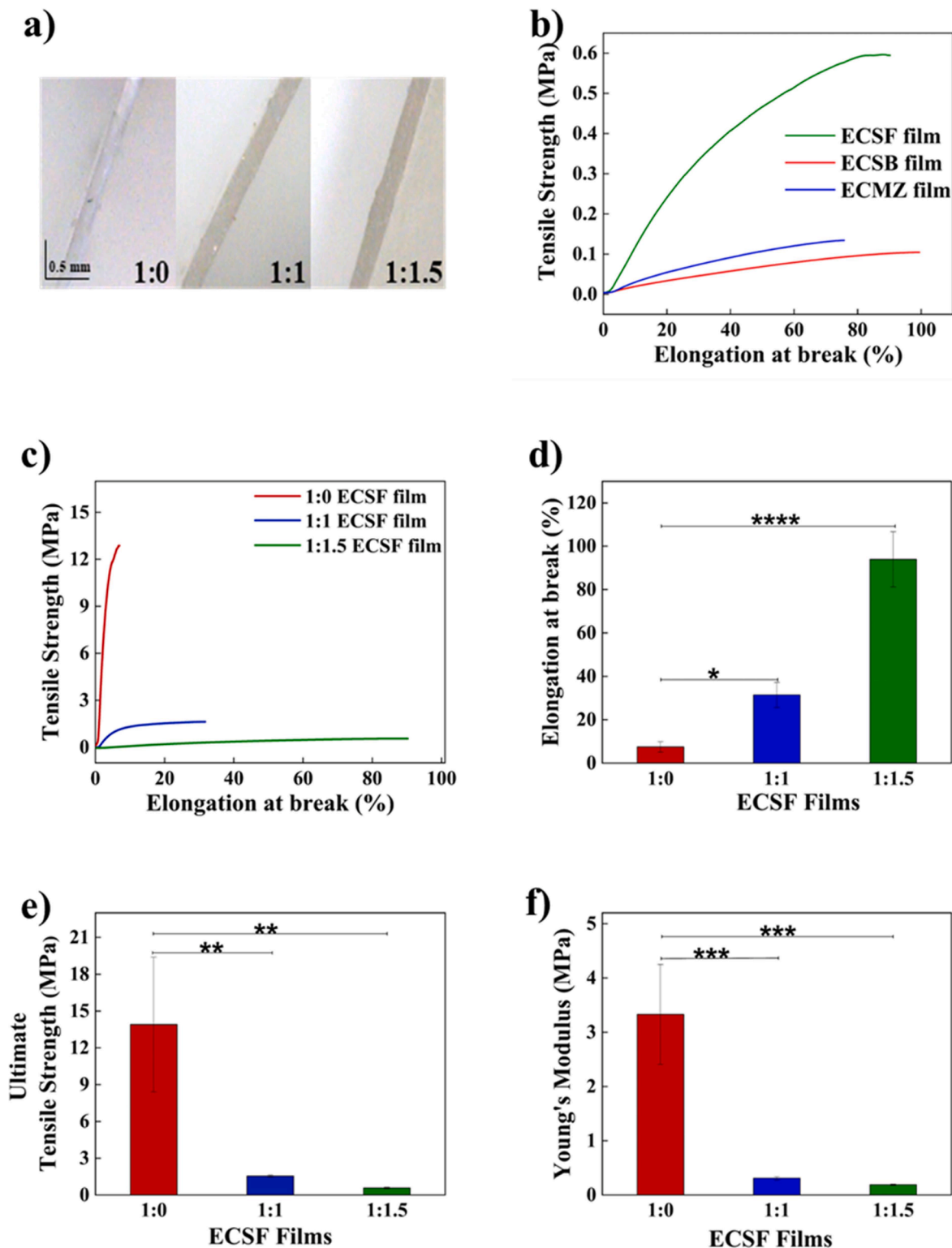


Fig. 4. a) Thickness of ECSF films b) Stress-Strain graph of EC: Oil films with different vegetable oils c) Stress-Strain graph of ECSF films, mechanical characterization results of different ratios of ECSF films - d) Elongation at the break e) Ultimate tensile strength and f) Young's modulus.

### 2.3. Characterizations

#### 2.3.1. Mechanical characterizations

The mechanical properties were measured at room temperature using uniaxial tensile testing using a Zwick/Roell universal testing machine (Ulm, Germany). Before the tensile strength tests, the thickness of

the ECSF films was measured using a Dino-Lite digital microscope (Taiwan, China). The films are cut into rectangular-shaped samples of length 27 mm and width 12.5 mm. The thickness of each film was determined using the microscope. The following Eqs. (1) & (2) were used for the mechanical tests.



**Table 2**

The results of mechanical characterization for different ratios of ECSF films—ultimate tensile strength, Young's modulus, and elongation at break were tabulated.

EC: SF oil ratio	Ultimate tensile strength (kPa)	Young's modulus (kPa)	Elongation at break (%)
1:0	13,900 ± 5400	3330 ± 920	7.5 ± 2.4
1:1	1550 ± 90	310 ± 30	31.4 ± 5.8
1:1.5	580 ± 50	190 ± 10	93.9 ± 12.0

**Table 3**

Effect on stretchability of ethyl cellulose films plasticized using various natural compounds.

Plasticizer	Steps involved	Solvents	Elongation at break (%)	Reference
Triethyl citrate	Single step	Cetyl alcohol	11.04 ± 1.85	(Frohoff-Hülsmann et al., 1999)
Epoxidized soybean oil	Single step	Acetone	13.0 ± 0.40	(Yang et al., 2014)
Dimeric Acid	Multi step	Chloroform	87 ± 4.00	(Lee et al., 2015)
Polylols	Multi step	Acetic acid	21.84 ± 2.07	(Lin, Li et al., 2021)
Lipoic acid	Single step	Acetic acid	46.03 ± 0.07	(Lin, Asante et al., 2021)
Thioether polyol	Multi step	Acetic acid	43.37 ± 4.39	(Yan et al., 2023)
Transesterified sunflower oil	Single step	Ethanol	93.89 ± 12.00	Our work

$$\text{Cross sectional area} = \text{Thickness} \times \text{Width} \quad (1)$$

$$\text{Stress} = \frac{\text{Force}}{\text{Crosssectional area}} \quad (2)$$

A velocity of 10 mm/min was applied within the load range of 100 N for the measurements. Triplicate measurements were carried out and an average value was taken.

### 2.3.2. Rheological characterizations

Rheology experiments were carried out using Malvern Kinexus Pro+ Rheometer (Worcestershire, UK). An aluminium parallel plate of 20 mm diameter was used as the geometry. A Force of 0.2 N was applied on each sample film throughout the measurements to avoid the slipping of films from their defined position. The only exception was made for 1:0 EC: Oil film in which a force of 10 N was applied to avoid slipping (the instrument was not enough to do the rheological test for the 1:0 film due to the slipping). First, an amplitude sweep test was conducted at a constant frequency of 1 Hz with a varying strain from 0.01 % to 50 % to identify the linear viscoelastic region. Secondly, oscillation frequency sweep tests were achieved for each sample at a constant strain of 1 % while varying the frequency range from 0.1 to 100 Hz. Both tests were performed at 37 °C. The rheological test in the liquid form was not performed, since the ECSF solution was prepared in ethanol solvent, and it will start getting evaporate during the synthesis which will lead to inaccurate data.

The density of the elastic chain present in the ECSF films of the different ratios was calculated by the Flory equation, which is given by,

$$\sigma = \rho_{xe} RT \left( \alpha - \frac{1}{\alpha^2} \right) = G^* \left( \alpha - \frac{1}{\alpha^2} \right) \quad (3)$$

Where,  $\sigma$  is the uniaxial compressive stress,  $\alpha = L / L_i$ , with L the actual thickness of the compressed sample and  $L_i$  the initial thickness of the sample, R is the universal gas constant, and T is the absolute temperature.  $\rho_{xe}$  represents the moles of elastically effective chains per  $\text{dm}^3$  of the dry polymer network and  $G^*$  is the complex shear modulus of the swollen network.

### 2.3.3. Fourier transform infrared spectroscopy (FTIR) analysis

The resultant ECSF films without any modification were subjected to FTIR analysis to determine the functional groups. The measurements were taken by Perkin Elmer Spectrum two FTIR spectrometer (Waltham, USA) in the range of 4500–450  $\text{cm}^{-1}$  with the resolution 4  $\text{cm}^{-1}$ .

### 2.3.4. X-Ray diffraction (XRD) analysis

The change in the crystallinity for the ECSF films compared to pure ethyl cellulose was analysed by X-ray diffraction technique. The measurements were done with a Rigaku Ultima X-ray diffractometer (Rigaku, Tokyo, Japan) using monochromatic Cu K $\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) operating at 40 kV and 20 mA. The diffractogram was recorded at a scanning rate of 0.02°  $\text{min}^{-1}$  in the angle range between 2° and 50°. The degree of crystallinity index of the ECSF films was determined using the equation,

$$\text{CI}(\%) = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks}} \times 100 \quad (4)$$

### 2.3.5. Thermogravimetric analysis (TGA)

The thermogravimetric analyser TA SDT - Q600 (New Castle, DE, USA) was used to examine the thermal stability of the synthesized ECSF films. The samples were heated in an aluminium pan at a scanning rate of 10 °C  $\text{min}^{-1}$  within the temperature range of 10 °C – 550 °C under the nitrogen atmosphere at a 50 mL/min flow rate.

### 2.3.6. Morphological analysis

The morphological characterization of ECSF films was performed by Zeiss Field-emission Scanning Electron Microscope (FESEM), (Sigma VP, Carl Zeiss, Jena, Germany) with an accelerating voltage of 10 kV. The distance between the sample and the SEM aperture was 0.95 cm. All the samples were directly subjected to SEM analysis without any modification.

### 2.3.7. Contact angle measurements

The hydrophobicity of ECSF films of different ratios was determined by First Ten Angstroms, FTA 1000 software (Newark, California, USA) equipped with a CDD camera using the sessile drop method at room temperature. The static contact angle between the water droplet and the film was measured. Five measurements for each film were done in different positions and an average value was calculated.

### 2.3.8. Preliminary dip coating on strawberries

The strawberries purchased from the supermarket were dip-coated in the ECSF solution three times for 30 seconds and then allowed to evaporate the solution at room temperature. The analysis was carried out for one week. In parallel strawberries without dip coating in ECSF solution were used as a control. The quality of both sets of strawberries was noted by evaluating their weight loss during the storage times. Triplicate measurements were carried out.

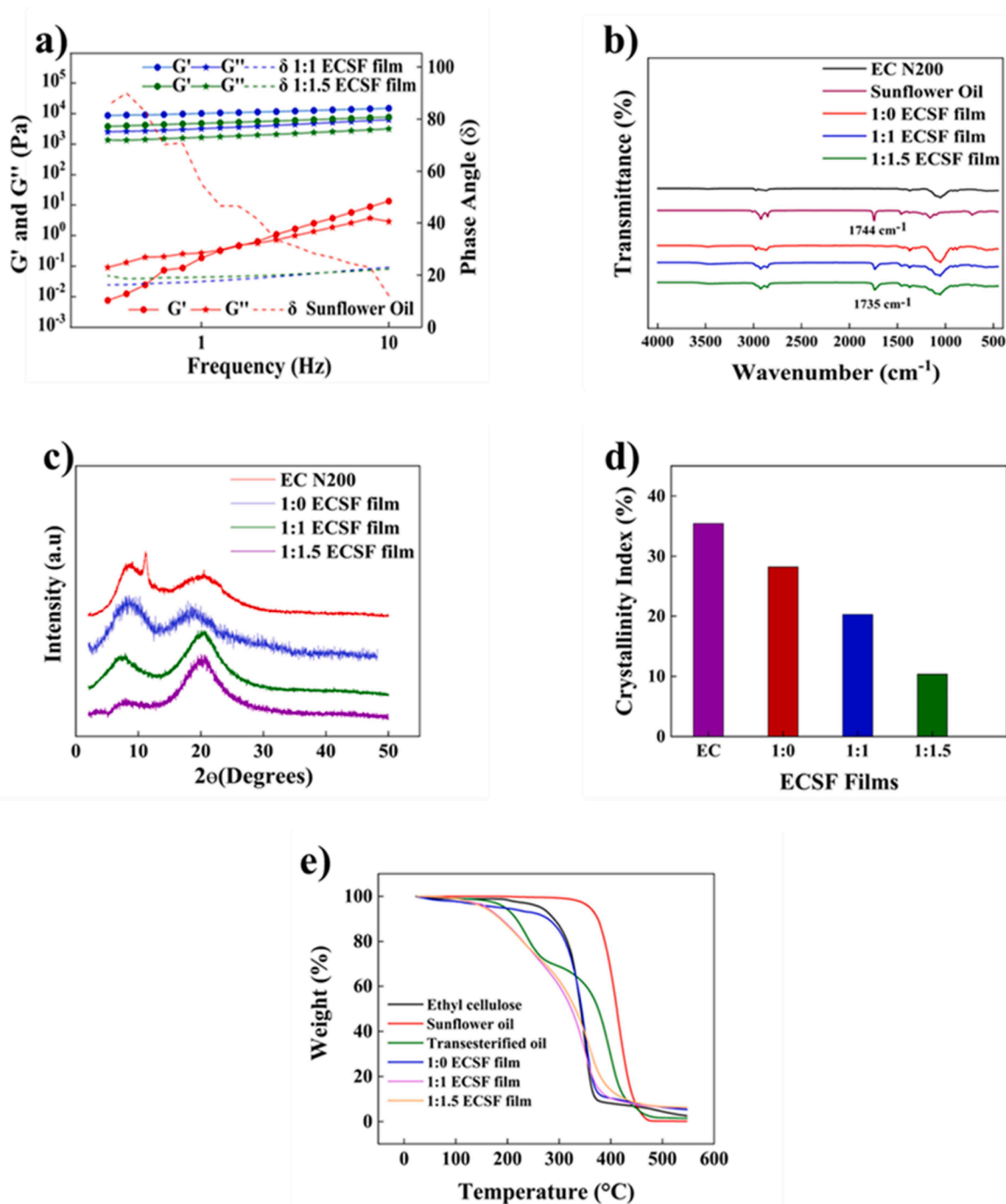
### 2.3.9. Statistical analysis

All the experiments were conducted in triplicate for each sample. GraphPad Prism 8 - ONE WAY ANOVA software and Microsoft Excel were used to examine the statistical data. The arithmetic means and standard deviation was used to display the results. Results were analysed using the *t*-test with a significance level of  $p < 0.05$ .

## 3. Results and discussion

### 3.1. Synthesis of ECSF films

The ECSF films were produced by plasticizing the ethyl cellulose with transesterified sunflower oil. The transesterification reaction is a simple reversible organic reaction, mostly applied for biodiesel production (Anastopoulos et al., 2009; E. Khan et al., 2023; Mandari &



**Fig. 5.** a) Rheological analysis- oscillation frequency sweep result of ECSF films- elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ), b) FTIR spectra of ECSF films, c) XRD diffractogram of ECSF films, d) Decrease in crystallinity index of ECSF films and e) Thermogravimetric analysis of ECSF films.

Devarai, 2022), and is defined as an equilibrium reaction in which an ester is transformed into another through the interchange of alkoxy moiety (Mandari & Devarai, 2022). The rate of the transesterification reaction can be accelerated in the presence of acid or base catalysts. The synthesis protocol and the mechanism of transesterification are depicted in Fig. 2, Schemes 1a and 2, respectively. NaOH is confirmed as a superior catalyst for the transesterification reaction usually applied for biodiesel production (Rashid et al., 2008; Vicente et al., 2004). With respect to the molecular weight, the NaOH has 40.01 g/mol compared to other catalyst such as KOH (56.11 g/mol) and  $\text{CH}_3\text{ONa}$  (54.04 g/mol). It is presumed that all catalysts are equally effective on a molar basis because each mol of catalyst produces one mol of the alkoxide anion

(first step of mechanism Scheme 1). The molecular weights order suggests that the order of efficacy by mass would be  $\text{NaOH} > \text{CH}_3\text{ONa} > \text{KOH}$  (Pullen & Saeed, 2015). Moreover, NaOH is cost-effective and used as a food additive.

Briefly, the mechanism of the transesterification reaction involves initially, reaction of NaOH with ethanol to form an ethoxide ion which exhibits higher reactivity compared to the hydroxide ion. This ethoxide ion then facilitates the transesterification of triglycerides present in the sunflower oil, initially forming one fatty acid ethyl ester and diglycerides. This diglyceride undergoes the same mechanism followed by monoglyceride to obtain three different fatty acid ethyl esters and glycerol as final products. The ethyl cellulose was then allowed to

**Table 4**

The FTIR peak values of ethyl cellulose and sunflower oil were observed in spectra.

Compound	Peak value (cm <sup>-1</sup> )	Characteristic vibration
Ethyl Cellulose	3475	-OH stretching
	2974	-CH asymmetric stretching
	2869	-CH symmetric stretching
	1374	-CH symmetric bending
	1052	-C-O-C symmetric stretching
Sunflower Oil	3009	=CH stretching
	2923	-CH <sub>2</sub> asymmetric stretching
	2869	-CH <sub>2</sub> symmetric stretching
	1461	-CH <sub>2</sub> bending or in-plane -OH stretching
	1237	Aliphatic -C-O-C- stretching
	1160 and 1096	-C-O bending
	721	-CH <sub>2</sub> rocking

interact with the transesterified products of sunflower oil. The interaction between the plasticizer and ethyl cellulose was considered a non-covalent supramolecular interaction in which the hydroxyl group of ethyl cellulose interacts with the carbonyl groups of the fatty acid ethyl esters via H-bonding (Schemes 1b and 3). It is possible to visually understand when the transesterification reaction between sunflower oil and ethanol has happened because the initial emulsion shifts to a slightly yellow homogenous solution (Figure.S1). We have used a molar ratio of 1:10 between oil and ethanol for the transesterification reaction (Domingos et al., 2008).

Among the four ECSF films synthesized with different EC: Oil ratios (1:0, 1:0.5, 1:1, 1–1.5, and 1:2), oil phase separation was visible by the eye starting from the EC: Oil ratio of 1:2. At this ratio, the transesterified sunflower oil concentration becomes supersaturated and thus gets started to leach out from the EC matrices. In addition, imperfections like bubbles and holes (Figures S3 and S4) were observed in the films due to the partial phase separation which arises from the aggregation of non-transesterified sunflower oil in the EC matrices and hence resulted in uneven surfaces (Chan et al., 2005). Differently, for ratios lower than 1:2 except the 1:0 ratio, the obtained ECSF films plasticized with transesterified sunflower oil after the transesterification was transparent (Fig. 3). Thus, from the synthesized films, the maximum EC: Oil ratio of ECSF film that can be obtained without phase separation was 1:1.5. Hence, the concentration of transesterified sunflower oil that can saturate the EC polymer matrices is 1.5 times the EC content. Thus, the films

with EC: Oil ratios of 1:0, 1:1, and 1:1.5 were subjected to different characterizations.

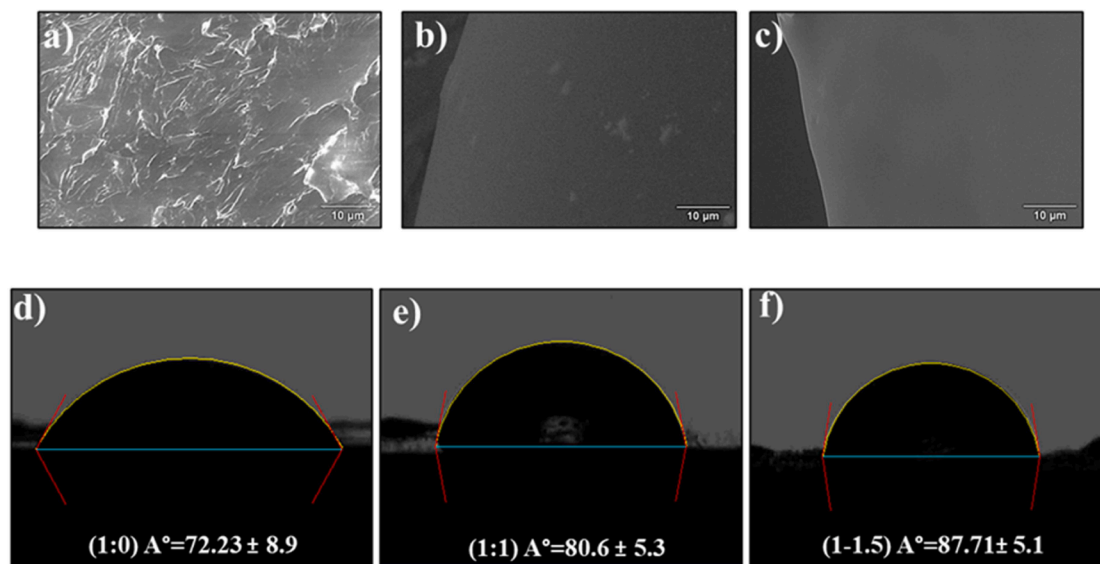
As a control, we produced the 1:1.5 ECSF\* films plasticized with sunflower oil in the absence of NaOH but exhibited an oil phase separation, and the resulting film surface was clearly uneven (Figure.S5) while the EC films plasticized with different transesterified vegetable oils were transparent with even surface. Consequently, in the case of 1:1.5 ECSF\* films, we can suppose that the alcohol and sunflower oil are not miscible each other even at 50 °C and confirms that no transesterification reaction happened (Figure.S6–S8). It implies that the small molecules produced from the transesterification of sunflower oil show a higher affinity towards ethyl cellulose, preventing the oil phase separation from the ECSF films.

### 3.2. Mechanical characterization

The thickness for all the ECSF films was measured and a thickness of ~100 μm, ~140 μm and ~160 μm was observed for 1:0, 1:1 and 1:1.5 ECSF films respectively (Fig. 4a). The addition of transesterified sunflower oil increased the thickness of the films, suggesting that the thickness is proportional to the concentration of transesterified sunflower oil. A preliminary comparison between the mechanical properties of 1:1.5 ethyl cellulose films plasticized with different vegetable oils was performed to select the best-performing oil-based film in terms of ultimate tensile strength and elongation at the break (Fig. 4b). Sunflower oil-based films showed the best performance between elongation and ultimate tensile strength about ~94 % and ~580 kPa respectively then it was selected for further characterization. A lower value of ultimate tensile strength was observed for both transesterified maize (ECMZ) and soybean (ECSB) oil-plasticized EC films at about ~100-110 kPa and the lowest elongation at break was exhibited by ECSB films at about ~72 %. The mechanical properties of EC films plasticized with different transesterified vegetable oil was summarized in Table S1.

The successive mechanical studies of the ECSF films showed that as the amount of transesterified sunflower oil increases, the elongation at the break of the films also increases with a decrease in tensile strength (Fig. 4c, Table 2).

The 1:1.5 ECSF film has shown elongation at break and ultimate tensile strength of about ~94 % and ~580 kPa respectively (Fig. 4d and e). Young's modulus of 1:1.5 ECSF film has decreased by ~94 % as compared to 1:0 ECSF film (Fig. 4f). A decrease in tensile strength and an increase in deformation of the ECSF films confirms that the addition of



**Fig. 6.** SEM image of ECSF film a) 1:0 ratio b) 1:1 ratio and c) 1:1.5 ratio (the black surface represents the plane of the sample chamber where the specimen gets mounted for the analysis) Contact Angle images ECSF films d) 1:0 ratio e) 1:1 ratio and f) 1:1.5 ratio.



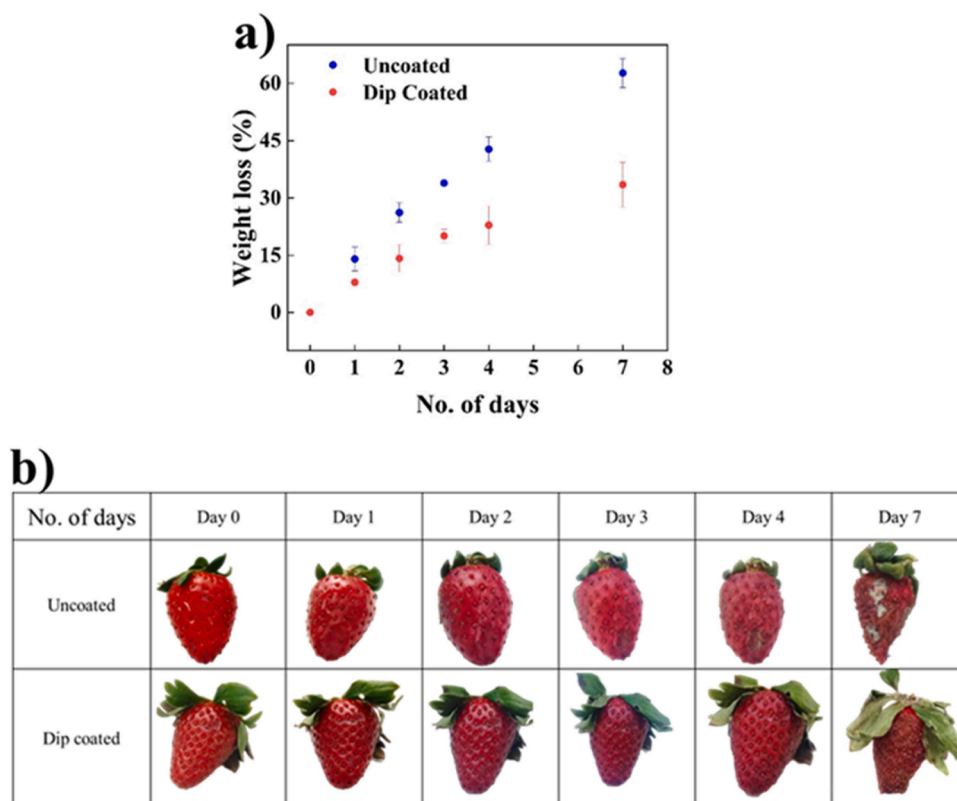


Fig. 7. a) The percentage of weight loss for each set of strawberries (uncoated and dip-coated) with the various storage times and b) The external appearance of both uncoated and dip-coated strawberries at various storage times.

transesterified sunflower oil reduces the stiffness and provides softness to the films, respectively. The physical properties of all ECSF films are summarized in Table S2. Moreover, Table 3 describes the plasticizers that were explored for ethyl cellulose in literature and their effect on the mechanical properties which can be used to compare the mechanical analysis results of ECSF film.

The fatty acid ethyl esters produced from the transesterification interact with the gel sites present in the EC polymer matrix, responsible for the stiffness of the polymer, and separate them from adjacent polymer chains by weakening the H-bond and hydrophobic interaction, then create new non-covalent interactions. Thus, a supramolecular complex system established between ethyl cellulose and transesterified sunflower oil can provide back-and-forth gliding movement within the matrix.

### 3.3. Rheological characterizations

The rheological results provide insight into the viscoelastic nature of these materials and their molecular behaviour. In all the ECSF films, the storage modulus ( $G'$ ) was found to be greater than the loss modulus ( $G''$ ), indicating more elastic-like behaviour than viscous at 37 °C. These results confirmed that the viscoelastic behaviour of the films was predominantly dominated by a solid-like nature. This higher elastic behaviour was also confirmed by the phase angle ( $\delta$ ) which appeared below 45°. Furthermore, an increase in  $G'$  similar to  $G''$  was observed with an increase in frequency, suggesting that the ECSF films possess frequency-dependent viscoelasticity and hence behave like a non-Newtonian fluid (Fig. 5a). The 1:0 ECSF film which has shown a higher stiffness from the mechanical tensile strength test, was quite difficult to perform the rheological analysis in the same conditions with the instrument due to the film slipping.

The density of the elastic chain ( $\rho_{xe}$ ) present in the ECSF films of different ratios was calculated using the Flory equation (Flory, 1953)

and it ranges from 4.68 to 2.29 (detail in material and method). A lower density of elastic chain was obtained for 1:1.5 ECSF film, which indicates the improved ability of the film for elongation. These data confirm what was observed in the mechanical characterizations, where an elastic modulus reduction was observed with increasing transesterified sunflower oil content, primarily due to the decrease in the density of elastically active chains.

### 3.4. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR analysis was performed to evaluate the chemical fingerprint of the material. In particular, a peak at 1735  $\text{cm}^{-1}$  was observed, indicating the presence of new ester carbonyl groups typical of ethyl esters of fatty acids generated from the transesterification of sunflower oil (Fig. 5b). A sharp peak at 1744  $\text{cm}^{-1}$  in spectra of pure sunflower oil corresponds to the C=O stretching of ester groups on triglycerides (Gorade et al., 2019). The difference in the frequency of ester carbonyl peak values arises from different degrees of substitution due to the transesterification reaction (Uschanov et al., 2011). Jandura et al. have reported that the intensity of the carbonyl peak is directly proportional to the degree of substitution (Jandura et al., 2000; Lease et al., 2021; Onwukamike et al., 2018). The intensity of the carbonyl peak is ascribed to the transesterification rate of sunflower oil. The intensity represents how much fatty acid ethyl esters were formed by substituting the acyl group of triglycerides with the ethoxy group. The shift of the ester carbonyl peak from 1744  $\text{cm}^{-1}$  to 1735  $\text{cm}^{-1}$  suggests the change in the environment of ester carbonyl groups from triglycerides which proves that transesterification of sunflower oil was successful (Gorade et al., 2019). The peaks observed for pure ethyl cellulose and sunflower oil in the FTIR spectrum were tabulated (Table 4).

The FTIR spectra show that most of the peaks shown by the ECSF films are derived from pure ethyl cellulose, suggesting that the produced

fatty acid ethyl esters were not reacted with the hydroxyl groups of ethyl cellulose, hence, no chemical modification occurred on EC chains. The further transesterification reaction of fatty acid ethyl esters (produced from the first transesterification of sunflower oil) with the ethyl cellulose was known to hardly occur at room temperature due to its surface nature and generally low content of reaction, which results a very weak ester carbonyl peak (Dankovich & Hsieh, 2007).

### 3.5. X-ray diffraction (XRD) analysis

The XRD results of the ECSF films show a change in the crystallinity region within the EC matrix compared to the pure ethyl cellulose. The diffraction peaks observed for different ECSF films and the degree of crystallinity were determined. A sharp peak was observed for EC N200 at  $2\theta = 11.26^\circ$  on the other hand, a broad peak was observed for the ECSF films at  $2\theta = 8.46^\circ$ ,  $7.42^\circ$  and  $7.16^\circ$  for 1:0, 1:1 and 1:1.5 ECSF films, respectively (Fig. 5c). The diffractogram showed that diffraction peak intensity decreased with an increase in transesterified sunflower oil concentration. The addition of transesterified sunflower oil decreases the degree of crystallinity by changing the original structure of the ethyl cellulose through the newly formed fatty acid ethyl esters which fabricate new intermolecular connections within the EC polymer, loosens the H-bonding interactions and make the EC chains more flexible. They get incorporated within the EC matrix and glide over EC chains, hence diminishing the crystallinity thereby creating more amorphous regions.

According to Eq. (2), which is covered in the XRD characterization method section, the crystallinity index (CI) percentage was computed. The crystallinity index (%) for EC N200 was  $\sim 35.44\%$  whereas for 1:0, 1:1, and 1:1.5 ECSF films were  $\sim 28.21\%$ ,  $\sim 20.27\%$ , and  $\sim 10.36\%$  respectively which confirms that the addition of transesterified sunflower oil decreased the crystallinity of EC (Fig. 5d). This drop in the crystallinity index has supported the decline in the tensile strength, as the decrease in crystallinity follows a decrease in tensile modulus.

### 3.6. Thermogravimetric analysis (TGA)

The TGA analysis demonstrates sunflower oil transesterification. The pre-transesterification oil and post-transesterification oil exhibit distinct behaviours, notably showcasing a lower degradation temperature (Fig. 5e). The transesterified sunflower oil began to decompose at  $\sim 150^\circ\text{C}$  while the sunflower oil began to degrade at  $\sim 300^\circ\text{C}$ . The initial degradation of the 1:1 and 1:1.5 ECSF films was noticed at a temperature close to the transesterified oil while the pure ethyl cellulose revealed a degradation at  $\sim 200^\circ\text{C}$ . The decrease in thermal stability is due to the thermal interference in the molecular interactions (M. Li et al., 2017). It is explained as the heat flow disrupts the non-covalent intermolecular H bonding forces between the fatty acid ethyl esters produced from the transesterification of sunflower oil and the EC polymer leading to the overflow of them from the films (Lin, Asante et al., 2021; Lin, Li et al., 2021). However, the degradation temperature above  $100^\circ\text{C}$  demonstrates that the developed films can find applications in the fields of food packaging, drug delivery, and flexible wearable electronics.

### 3.7. Morphology analysis

The morphology of ethyl cellulose films after the plasticization with transesterified sunflower oil was analysed by SEM. The 1:1.5 ECSF film has shown a smooth-uniform surface throughout with no observable roughness and porosity as compared to the 1:0 ECSF film (Fig. 6a-c). The SEM images of the 1:1 ECSF film revealed that ethyl cellulose polymer matrices were unsaturated with the fatty acid ethyl ester, whereas the smooth surface of the 1:1.5 ECSF film confirmed that the saturation can be achieved with a concentration of sunflower oil, 1.5 times that of the EC amount. The presence of transesterified sunflower oil has influenced the smoothening of the EC surface, indicating that the

transesterification products of sunflower oil are completely miscible with EC and even distributed within the EC chains.

### 3.8. Contact angle measurements

The hydrophobicity of EC films has shown a dependence on the amount of transesterified sunflower oil added. The contact angles obtained for 1:0, 1:1, and 1:1.5 ECSF films were  $\sim 72^\circ$ ,  $\sim 80^\circ$ , and  $\sim 88^\circ$  respectively (Fig. 6d-f). An increase in the contact angle has been observed for 1:1 and 1:1.5 ECSF films with the addition of transesterified sunflower oil. Comparing 1:1 and 1:1.5 ECSF films to the pure 1:0 EC: Oil film, the percentage increase in contact angle was calculated to be  $\sim 12\%$  and  $\sim 21\%$ , respectively. Among those different ratios of ECSF films, 1:1.5 ECSF film has shown the most hydrophobic nature by forming the highest contact angle.

### 3.9. Preliminary dip coating on strawberries

Strawberries are a kind of fruit that contains quiet pores, delicate skin, and a high amount of water and sugar (Giampieri et al., 2012). These can soak up the moisture content from the surrounding environment easily, which leads to faster mould growth, commonly grey mould caused by the fungus *Botrytis cinerea* Pers (Iqbal et al., 2021). The outcomes of the dip coating showed that the strawberries that were dip-coated with the ECSF solution had better quality and protection than the uncoated ones. Fig. 7a depicts the graph of the percentage of weight loss with storage time for both sets. Comparing uncoated strawberries to dip-coated ones, the proportion of weight loss was approximately twice as high. After one week of storage time, we observed a weight loss of  $\sim 63 \pm 3.1\%$  for uncoated strawberries whereas about  $\sim 33 \pm 5.8\%$  for dip-coated strawberries. The external appearance of the dip-coated strawberries, which is depicted in Fig. 7b, indicates that they were shielded from mould growth for one week. The preliminary dip coating test produced positive and intriguing results for forthcoming antimicrobial research, and more characterisations will be carried out in the ensuing work.

## 4. Conclusion

The study evidenced that transesterified vegetable oils, and in particular sunflower oil, can function as EC plasticizers acting positively on elongation at breaks of EC films without the usual drawback related to green plasticizers such as phase separation, leakage, and low deformation. In particular, the transesterification reaction, driven by the strong base NaOH which served as a catalyst, boosted the development of a supramolecular system between ethyl cellulose and sunflower oil allowing to charge EC with a higher amount of a green plasticizer compared to control without phase separation. The fatty acid ethyl esters, di- and monoglycerides were found to be more affinitive towards EC than sunflower oil itself and the physical outcome of this effect was highlighted through the characterization. The experimental results demonstrated that transesterified sunflower oil could function as a good plasticizer for EC polymer to promote better stretchability by about  $\sim 94\%$ , as evidenced by the mechanical results of ECSF films. We have also verified this increase in stretchability due to the reduction of the elastic active chain as measured by the Flory equation through rheological characterization. The drop in the crystallinity index detected in the XRD studies proved the reduction in the tensile strength as well. The good affinity of transesterified products of sunflower oil towards EC and the saturated EC: Oil ratio as 1:1.5 were confirmed even with SEM analysis as indicated by the flat surface with non-observable roughness. The occurrence of a successful transesterification reaction of sunflower oil was confirmed by FTIR results as a shift in the ester carbonyl peaks from  $1744\text{ cm}^{-1}$  to  $1735\text{ cm}^{-1}$  was observed. The contact angle measurements of the films revealed the improved hydrophobic nature of ECSF film. Future antimicrobial studies of the films have been made possible by the

preliminary findings of the protection of strawberries obtained from the dip coating with ECSF solution.

In conclusion, the suggested synthesis was simple, straightforward, environmentally benign as well as cost-effective and the outcomes were satisfactory. This method of synthesis can be used to produce more ECSF films with various desirable properties for several applications including food packaging, transdermal drug delivery systems, and stretchable electronics.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.carpta.2023.100378](https://doi.org/10.1016/j.carpta.2023.100378).

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