

Plasticized Polyethylene/Chitosan Blend Films and Study of the Effect of Plasticizers on their various Properties and Biodegradability

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ABSTRACT

Chitosan (CH) and low-density polyethylene (PE) blend films were produced by a twin-screw extruder and heat press with different plasticizers glycerol (GLY), sorbitol (SOR) and polyethylene glycol (PEG). The tensile strength decreased and elongation at break increased with the incorporation of plasticizer for blends with 10 wt% of CH. The thermal stability of the films was slightly higher for films containing GLY and PEG as compared to SOR. Contact angles reduced from CH-PE film to the films containing PEG, SOR and GLY in decreasing order, respectively. Fourier transform infrared spectroscopy revealed no interactions between CH and PE in CH-PE film but, the addition of each plasticizer caused an interaction between CH and the plasticizer. CH-PE film containing PEG showed the smallest water vapor permeability. The heterogeneous structure of CH-PE film was improved with the addition of each plasticizer. CH-PE film containing SOR underwent biodegradation rate at a faster compared to the films containing GLY and PEG in soil burial end of 120 days. The lowest biodegradation rate was obtained in CH-PE film containing PEG, among the plasticized-films.

KEYWORDS : LDPE, Chitosan, Plasticizer, Extrusion, Biodegradability.

INTRODUCTION

Petroleum plastics are produced approximately 140 million tons each year, of which about 20-25% of plastics are converted into waste^[1]. As most of such plastics are non-biodegradable, such waste creates environmental problems. The environmental issue has motivated to search the alternative materials, such as natural polymers. Proteins and polysaccharides offer many advantages due to their biocompatibility, biodegradability and non-toxic properties. In 2009, the biopolymers were about 1% of the total polymer market but, it is estimated to reach 20% in 2020^[2].

Chitosan (CH) is the most important derivative of chitin after deacetylation by alkaline treatment. Chitin is the most widespread biopolymer in nature after cellulose which is obtained mainly from marine co-products, such as crabs, shrimps and the outer skeleton of insects, and also mushrooms and algae. It can be produced approximately 100 billion tons every year and it is used in different industrial areas such as biomedicine, water treatment and packaging. It has a good film-forming ability, good oxygen barrier and mechanical properties with antimicrobial activity and biodegradability. But, it is very sensitive to moisture^[3,4].

Polyethylene (PE) is one of the most important thermoplastics due to its low cost, high mechanical strength, good gas and humidity barrier properties, lightweight, ease of processing, excellent electrical insulation and chemical resistance. It has major environmental concern because of non-degradability under ambient condition^[1,2,3]. It is used in many applications such as packaging, protective coating on paper, textiles etc.

The blending of biopolymers and synthetic polymers represents a simple and economical way to combine their best properties along with the biodegradability of the obtain materials. The improved mechanical properties and antibacterial agent carrier in active packaging were obtained in polypropylene films coated with CH as observed by Hong et al.^[5]. The mechanical, barrier, thermal and microscopic properties of Poly-(ϵ -caprolactone)/CH films were examined by Joseph et al.^[6]. The thermal and mechanical properties were improved with the palm oil as a plasticizer incorporated into LDPE/CH blend films and the biodegradation rate increased with increasing CH concentration⁷.

Plasticizers are needed to improve the elasticity of the films by reducing the intermolecular forces. The different non-volatile plasticizers such as glycerol (GLY), sorbitol (SOR) and polyethylene glycol (PEG) and lipids are commonly used in CH-based films^[8-10]. The biodegradable films are generally produced by solvent casting method^[11,12]. But, extrusion and mixing^[8,13,14] techniques are preferred in the industry due to the high productivity and minimal space requirements.

There is not much information in the literature at present on the effect of sorbitol, glycerol and PEG on the CH-PE blend films. However, pure CH films are produced only via solvent casting method, the films from blending of CH with a thermoplastic polymer such as LDPE are obtained from many techniques, such as extrusion, mixing. Pure CH films are more sensitive to water vapor and limit the application for food packaging, the blend with hydrophobic polymer such as LDPE is a common method to get an optimum water vapor barrier

property^[2]. The negative impact on the environment of pure LDPE films can be reduced by blending it with a biodegradable polymer such as CH. Thus the aim of this study was to make a comprehensive study comparing the effects of different plasticizers such as GLY, SOR and PEG on the properties of CH-PE blend films. The CH-PE blend films, in this investigation, were prepared from low-density polyethylene and chitosan using a hot press and the blend pellets (obtained from the twin-screw extruder). The obtained blend films properties were examined for potential applications in food packaging.

($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, Av.Mw: 8000g/mol) were purchased from Merck, Sigma and Aldrich respectively.

Preparation of films

PE granules and CH powder were dried overnight in a vacuum oven at 80°C before extrusion. The films were produced in two steps. (1) The blend was firstly extruded by a twin-screw extruder (DSM Xplore 15 ml Micro-compounder) to pelletize with a temperature 135°C and 100 rpm. The feeding of the blends to the extruder as follows: CH powder and plasticizer was mixed in a cup before extrusion, half of PE granules were fed first to the extruder, all CH-plasticizer blends were fed immediately afterwards. The remaining PE granules were fed to the extruder and feeding ended. (2) The pellets from the extruder were placed into a hydraulic press at 135°C, 60 bar and 3min to obtain the films. Table 1 indicates the composition of each sample. According to the tensile test results, the 10CH/PE blend was chosen to examine the plasticizer effect. The weight ratio of plasticizer and chitosan in each film composition was kept as 1.0. The film thicknesses were measured with a micrometer (Mitutoyo-Model no: CD-15APX) with a precision of 0.01mm by averaging five measurements at different locations of the film.

EXPERIMENTAL

Materials

LDPE (density: 0.918g/cm³, MFI: 7.7 g/10min (190°C, 2.16kg) was supplied from Dow Chemical Company. CH with a deacetylation degree of ≥75 %, was purchased from Sigma-Aldrich. Glycerol (GLY) (C₃H₈O₃, Mw=92 g/mol), D-Sorbitol (SOR) (C₆H₁₄O₆, Mw=182.17g/mol) and Polyethylene glycol (PEG)

Characterization

TABLE 1. Compositions of PE/CH films

Sample	Composition of blends			Average film thickness (mm)
	PE (wt.%)	CH (wt.%)	Plasticizer (wt.%)	
PE film	100	0	0	0.22
5CH	95	5	0	0.24
10CH	90	10	0	0.17
15CH	85	15	0	0.30
20CH	80	20	0	0.18
10GLY1	90	5	5	0.21
10SOR1	90	5	5	0.23
10PEG1	90	5	5	0.26

Tensile tests were performed with a computer-controlled Instron Universal Testing Instrument (Model 3345K). The film samples were cut into strips that were 100mm in length by 20mm in width as to ASTM D882-12. The initial distance between the grips was 80mm and the crosshead speed was set at 10mm/min. The measurements were performed with the minimum of five replicates for each film and obtained the average.

Thermogravimetric analysis (TGA) was carried out with Mettler Toledo TGA 1 instrument. Samples between 5-10mg were taken and heated from 25°C to 750°C at the heating rate 10°C/min under 50 mL/min nitrogen gas flow.

The surface hydrophilicity-hydrophobicity of the films was determined with an Attention Theta Lite CA(contact angle) instrument. 5 μ l of distilled water was placed on the surface of the film by a micro-syringe. Ten images were obtained at 1second interval for each droplet. At least five measurements were taken to get the average CA at different positions. Fourier-transform infrared spectroscopic analyses of the films were carried out using FTIR Perkin-Elmer 100 spectrophotometer in transmittance mode from 4000cm⁻¹ to 650cm⁻¹. The attenuated total reflectance (ATR) technique was applied with the diamond crystal to obtain FTIR spectra of the samples.

The water vapor permeability (WVP) through films was determined gravimetrically with ASTM Method E-96. The films were mounted over the test cups containing distilled water. The cups were placed in an environmental chamber at 25°C and 34-35 % RH. The cup weights were recorded every two hours for a total of between 60-72hr. Weight loss was measured as a function of time to calculate the water vapour transmission rate(WVTR). WVP (gm⁻¹s⁻¹Pa⁻¹) was calculated by multiplying WVTR by film thickness(m).

The surface morphology of the films was investigated by scanning electron microscopy (SEM), FEI –Quanta 400F. The instrument was operated at a constant voltage of 20kV. The films were coated with gold-palladium(3nm). 5000X magnification was used in the evaluation.

The biodegradation test of the films was carried out by the burial method as specified by Prasanna et al.^[15]. The film samples were buried in vegetable waste and bird manure-based compost. The humidity of the compost was maintained approximately 65% by adding water. The samples were buried into the wet compost at a depth 10cm. The samples were removed from the compost at 10 days interval and washed with distilled water and dried in an oven at 60°C to fixed weight. The weight loss was recorded with regard to time as a measure of biodegradation. The test lasted 120 days.

RESULTS AND DISCUSSION

Mechanical Properties

The blend films were prepared with 5, 10, 15 and 20 wt.% of CH into PE to determine the optimum weight percent (wt %) of CH at the beginning of this study. Fig.1a and b show the effect of the CH concentrations on tensile strength (TS) and elongation at break (EAB). The addition of 5 %,10 %,15 % and 20 wt.% of CH led to a decrease in TS of 6.3 MPa, 6.2 MPa, 4.6 MPa and 3.7 MPa, respectively. EAB values changed with the addition of 5%, 10 %,15 % and 20 % of CH into PE film from 43.3 % to 14.2 %, 11.0 %, 9.7 % and 6.7%, respectively. TS values were not presented a substantial change between 5 wt.% and 10 wt.% of CH incorporation into PE film and higher than 15 wt.% and 20 wt.% of CH into PE film. CH composition as 10 wt.% (10CH) was selected based on these data and this composition used to produce the films containing all plasticizers. Park et al., explained that LDPE has a crystalline structure and the lactate molecules of chitosan disrupt the crystalline structure of LDPE-CH blend films. They stated that the reason for decreasing effect in EAB with increasing concentration of CH was due to the reduction of polymer mobility^[16].

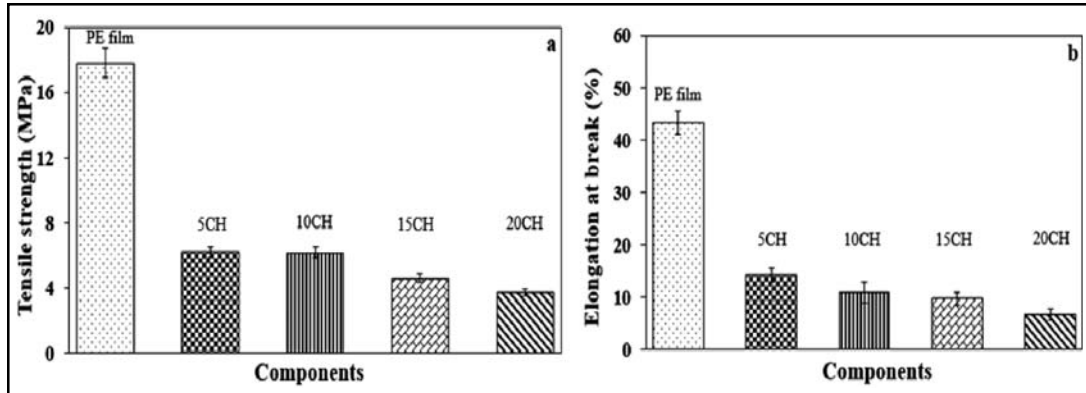


Fig. 1. Tensile strength and elongation at break of PE/CH films without plasticizer

Fig. 2. Shows the change in mechanical properties with the incorporation of three different plasticizers (GLY, SOR and PEG) to 10CH film. Tensile strength decreased with the addition of 10 wt.% of CH in PE without plasticizer with respect to PE film from 17.8 MPa to 6.2MPa as shown in Fig.2a. Tensile strength was showed a slight decrease by the incorporation of plasticizer into 10CH film regardless of which type of plasticizer used. These values were obtained 5.8MPa, 5.7MPa and 5.5MPa with the incorporation of GLY, SOR and PEG, respectively. This decrease in tensile strength is due to the reduction in intermolecular

interactions with the addition of plasticizer. Bourtoom studied rice starch/CH films with the incorporation of the plasticizers namely GLY, SOR and PEG. The starch/CH film containing SOR had higher tensile strength and lower elongation at break among the others. It was explained that the difficult interactions and fewer interruptions between rice starch/CH molecules due to the ring structure of SOR^[11].

EAB was sharply decreased with the incorporation of 10 wt.% of CH into PE from 43.3% to 11.0% as shown in Fig. 2b. The addition of plasticizer into the polymer matrix

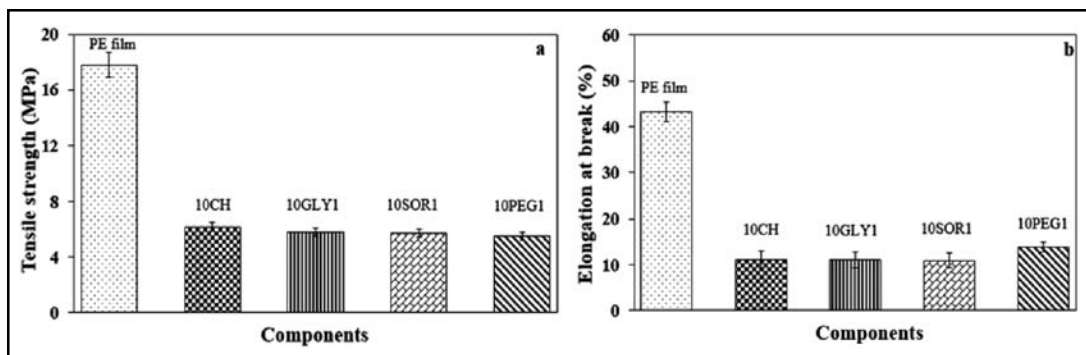


Fig. 2. Tensile strength and elongation at break of PE, 10CH and 10CH with plasticizer films

increases EAB. The increase was observed in 10CH film with all plasticizer type as shown in Fig. 2b. The EAB of 10CH film containing GLY, SOR and PEG were obtained as 11.2%, 11.0% and 13.9%, respectively. EAB of the 10CH film containing PEG was higher than 10 CH films containing other plasticizers. The difference in the mechanical properties in the blend films containing different plasticizers caused by the size, structure and shape of the plasticizer and the interaction between polymer chains.

Thermogravimetric Analysis

TGA is performed for the thermal stability of the films. Fig. 3 represents TGA curves of PE film, CH powder and blend films. $T_{5\%}$ and $T_{50\%}$ values show the temperatures at which 5% and 50% of the films degrade, as shown in Table 2. The maximum degradation temperatures from the first derivative curves for one, two or three stages are indicated in Table 2 as T_{dmax1} , T_{dmax2} and T_{dmax3} with the total ash weight. PE film shows single-stage degradation and maximum

degradation temperature is characterized by -C-C- breaking and observed as 476.8°C. The CH powder shows two degradation temperatures. The below 80°C corresponds to the water evaporation. T_{dmax2} is ranged from 267°C to 650°C with 27% total ash. This is explained due to the dehydration of saccharide rings and the decomposition of acetylated and de-acetylated units of CH^[17].

In the presence of CH and each plasticizer in PE, thermal degradation showed earlier compared to PE film as shown in $T_{5\%}$, $T_{50\%}$ values of blend films were similar to PE film. It was explained that it could be PE degradation after the remaining 50% of the films^[8]. The degradation of 10CH film containing GLY was observed at 247.2°C and related to the evaporation of GLY. Leceta et al. found as 225°C^[18]. T_{dmax2} of 10CH film is 296.8°C that was decreased slightly with the addition of GLY, SOR and PEG as, 296.1°C, 294.6°C and 295.3°C, respectively. T_{dmax3} of 10CH film was changed from 473.1°C to 470.2°C, 468.7°C and

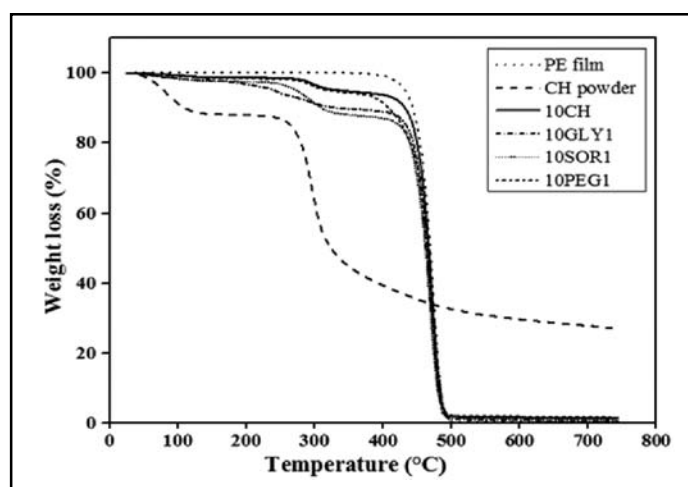


Fig. 3. TGA curves of PE/CH films

TABLE 2. TGA results of PE/CH films

Sample	T _{%5} (°C)	T _{%50} (°C)	T _{dmax1} (°C)	T _{dmax2} (°C)	T _{dmax3} (°C)	Ash weight %
PE film	432.3	469.0	-	-	476.8	0.4
CH powder	79.1	323.9	81.1	296.8	-	27.2
10CH	363.5	469.0	-	296.8	473.1	1.6
10GLY1	241.4	464.7	247.2	296.1	470.2	0.6
10SOR1	273.5	462.0	-	294.6	468.7	1.1
10PEG1	322.1	464.4	-	295.3	470.2	1.7

470.2°C with the addition of GLY, SOR and PEG, respectively. The observation is in agreement with the studies of Suyatma et al.^[19] and Kurek et. al.^[20]

The films containing GLY and PEG were observed a bit more thermal stable than the film containing SOR. While the ash amount was decreased with the addition of GLY and SOR, no change was observed with the addition of PEG as 1.7%.

Contact Angle

The angle (θ) between a horizontal film surface as a baseline and the water droplet is measured. CA is nearly zero that means water spreads over the film surface. On the other hand, the water droplet on the film surface places like a liquid ball that means CA is greater than 90° known as non-wetting^[21]. The hydrophilic and hydrophobic surfaces are defined quantitatively as $\theta < 65^\circ$ and $\theta > 65^\circ$, respectively^[22]. CA of hydrophobic materials such as LDPE film and plexiglass are stated as 93.9°-100.2°C and 91.5°C, respectively^[23]. CA of PE and blend films are represented in Fig. 4. PE film was found as

99.1°C which is in agreement with the literature^[23]. CA decreased with the addition of 10wt.% of CH as 98.5°. The biopolymers represent a hydrophilic nature as compared to synthetic polymers because they have many –OH groups that can bind with water molecules^[8].

CA more decreased with the addition of the plasticizer regardless of which type used. CA of the film containing PEG as 95° was nearby the film containing SOR as 94.9° and higher than the film containing GLY as 94.2°. Brzoska et al.^[24] explained that SOR is less hygroscopic compared to GLY and 71% soluble in water but, GLY is medium-high hygroscopicity and is infinitely soluble in water at 25°C. GLY higher absorbs and retains water compared to SOR due to its molecular weight. Generally, M_w of the polyols increases with decreasing hygroscopicity of polyols and leads the crystallization increases. M_w of PEG was greater than SOR and GLY. CA are affected by many parameters such as composition, surface roughness, surface charge, crystallinity and so on^[25].

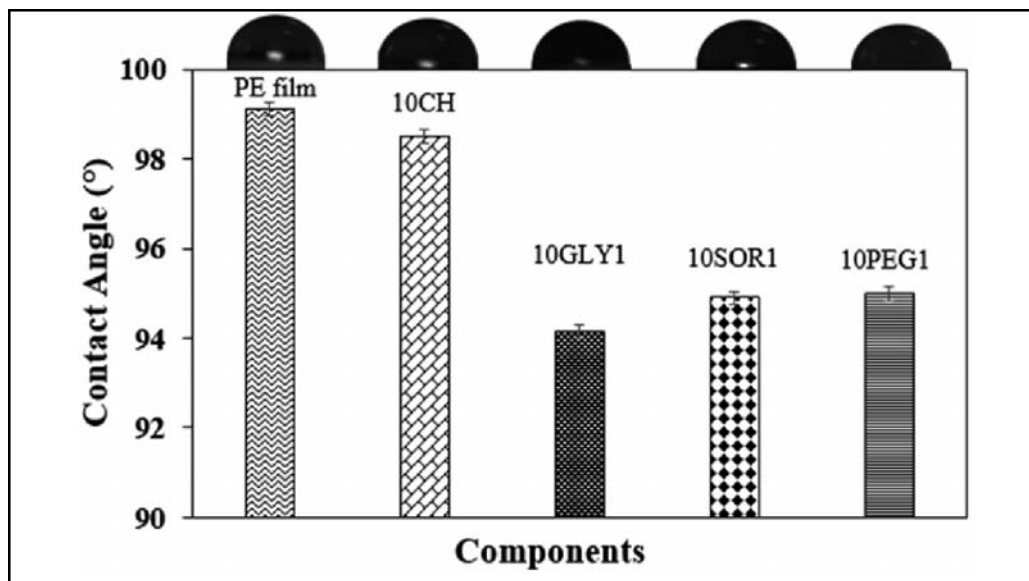


Fig. 4. CA of PE/CH films

Fourier Transform Infrared Spectroscopy

FTIR spectra of PE film, CH powder and blend films have been presented in Fig. 5 which shows the characteristic peaks of CH at 3350 cm^{-1} , 1640 cm^{-1} , 1572 cm^{-1} and 1070 cm^{-1} for inter and intramolecular hydrogen bonding between $-\text{OH}$ and $-\text{CH}_2\text{OH}$ groups, amide I amide II and carbonyl ($-\text{C}=\text{O}$) stretching, respectively^[15]. The main peaks of GLY were $-\text{OH}$ stretching at 3320 cm^{-1} , $-\text{CH}$ stretching at 2930 cm^{-1} and 2870 cm^{-1} , H_2O bending at 1652 cm^{-1} , $\text{C}-\text{O}-\text{H}$ bending at 1415 cm^{-1} , $\text{C}-\text{O}$ stretching from 1450 cm^{-1} (primary alcohol) to 1100 cm^{-1} (secondary alcohol) and $-\text{OH}$ bending 913 cm^{-1} ^[26]. The main peaks of SOR at 3300 cm^{-1} attributed to $-\text{OH}$ stretching and a peak at 2920 cm^{-1} $\text{C}-\text{H}$ stretching^[26]. FTIR spectrum of PEG indicated distinct peaks at 1240 cm^{-1} , 950 cm^{-1} , and 840 cm^{-1} ^[27].

The characteristic peaks of PE film at 2916 cm^{-1} and 2848 cm^{-1} attributed to $-\text{CH}_2$

symmetric stretching vibration, a peak at 1463 cm^{-1} indicating $-\text{CH}_3$ asymmetric stretching vibration and a peak at 718 cm^{-1} which correspond to $-\text{CH}_2$ rocking^[15], in Fig.5b. A new band or peak shift was not observed in the incorporation of CH into PE, it was noted that there was no chemical or physical interaction between them. A similar result was reported in the study by Quiroz-Castillo et al.^[28]. The incorporation of GLY into 10CH film (Fig. 5a), $\text{C}-\text{O}$ stretching at 1068 cm^{-1} shifted to 1082 cm^{-1} ; suggesting interactions between hydroxyl groups of CH and plasticizer by hydrogen bonding^[18]. The major change is the addition of SOR and PEG into 10CH film $\text{C}=\text{O}$ stretching at 1637 cm^{-1} shifted to 1651 cm^{-1} for both, is in agreement with the literature^[29,30]. A new small peak appeared at 1101 cm^{-1} in Fig. 5a for the 10CH film containing PEG.

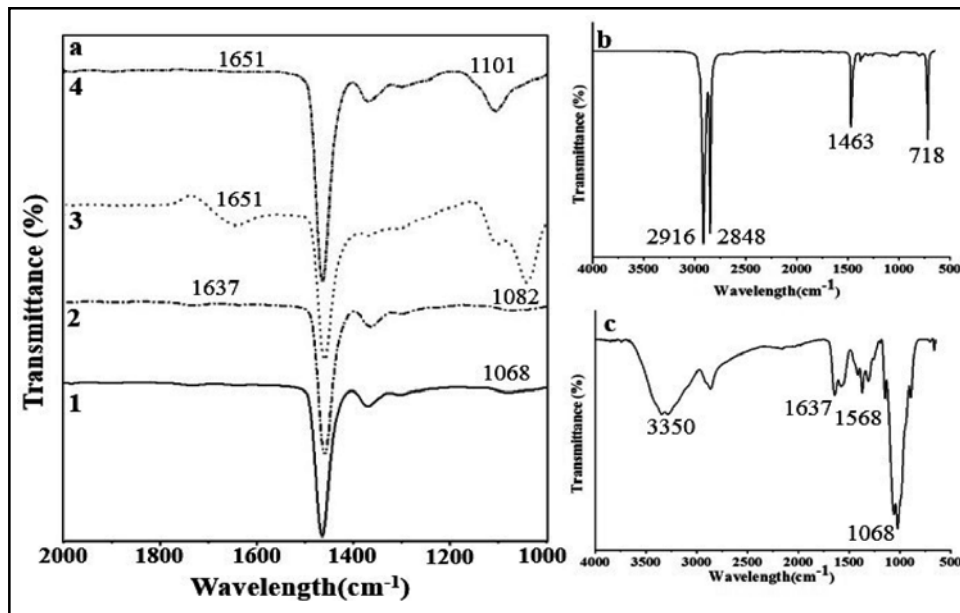


Fig. 5. FTIR spectra of a) 10CH(1), 10GLY1(2), 10SOR1(3), 10PEG1(4) b) PE film c) CH powder

Water Vapor Permeability

WVP is defined as the rate of transport of water vapor through the unit area of the film. WVP is a proportionality constant which is independent of the water vapor pressure difference through the hydrophobic polymer-based films like PE or polypropylene (PP). The biopolymers are hydrophilic polymers with polar groups that the groups interact with permeated water molecules. WVP is one of the important factors in food packaging. The permeated water vapor through packaging could spoil the food quality^[18,31].

The results of WVP are shown in Table 4. The CH addition in PE was increased nearly four times increase of the WVP. This could be explained by decrease integrity of PE film by CH lactate molecules and the effect of CH's hydrophilic nature^[16]. WVP was increased with the addition of the plasticizer regardless of which

type used. When GLY, SOR and PEG was added to 10CH film, WVP changed from $3.8 \times 10^{-11} \text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ to $13.8 \times 10^{-11} \text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$, $9.8 \times 10^{-11} \text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ and $2.8 \times 10^{-11} \text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$, respectively. Caner et al. reported that WVP increases with PEG addition to CH film^[32]. Farhan et al. reported the water barrier of semi-refined kappa-carrageen an film containing SOR is higher than film containing GLY^[26]. This result was observed in the study of Rodríguez-Núñez et. al.^[29]. They explained that it might be due to the SOR ring structure which may sterically hinder its insertion between the chains of CH, whereas GLY has a short linear chain, which is inserted and positioned within the three-dimensional polymer network. Park et al.^[33] reported the WVP of grain protein based-films containing GLY is higher than the films containing PEG. In this study, the best water barrier property was found in 10CH film

containing PEG among the films containing plasticizers. WVP of CH-PE film containing PEG showed lower value than that of CH-PE film containing SOR and GLY. This result was supported contact angle values, because CH-PE film containing PEG had the highest contact angle value as compared to the films containing SOR and GLY.

Morphological properties

Microstructural analysis of the film surfaces presented in Fig. 6. PE film had a homogeneous structure and no irregularity was detected as shown in Fig.6a. But, small CH domains were seen in PE matrix with the incorporation of CH in Fig.6b, but no coalescence of CH domains, in agreement with

TABLE 4. WVP of PE/CH films

Sample	WVP ($\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) $\times 10^{-11}$
PE film	1.1
10CH	3.8
10GLY1	13.8
10SOR1	9.8
10PEG1	2.8

the study⁸. 10CH film showed small CH in PE matrix a surface roughness due to the presence of the CH particles into PE matrix in Fig.6b. The heterogeneity of the films was slightly improved with the incorporation of all type plasticizer into 10CH film, it is in agreement with Rodríguez-Núñez et al.^[29].

Biodegradation

The biodegradation study of PE/CH films was measured by the burial test for a certain time^{15,34}. The samples of the PE/CH films were

buried into the compost for 120 days to determine their degradation. The percentage weight loss of the films versus the number of days was shown in Fig. 7. The weight loss was increased with the addition of CH to PE during 120 days, whereas PE film indicated no weight change within this period. The weight loss of 10CH film was obtained as 2.1% at the end of this period that is in agreement with the study of Prasanna et al.^[15]. They have explained that the CH was provided with the nutrient requirement for microbial growth in the degradation of LDPE/CH blends. The rate of weight loss of the films increased with the addition of plasticizer regardless of which type used. Sunilkumar et al.⁷ reported that the degradation increased with palm oil addition as a plasticizer to LDPE/CH film due to its wetting property and sensitivity to the fungi attack. The maximum weight loss approximately after 10 days presented then it continued slightly degradation up to the end of the time for all plasticized films. The fastest and maximum weight loss at the end of the period as 6.1% indicated in the 10CH film containing SOR. The weight loss of the films containing GLY and PEG were obtained as 4.9% and 3%, respectively at the end of this test.

CONCLUSIONS

The PE/CH blend films with different plasticizers (GLY, SOR and PEG) were prepared by extrusion and hot press techniques. The effect of different plasticizers was investigated on the structural, mechanical, thermal, WVP and biodegradability properties of the films. It can be concluded that tensile strength decreased with the addition of CH and plasticizer into PE. The film elongation properties were more affected by the addition

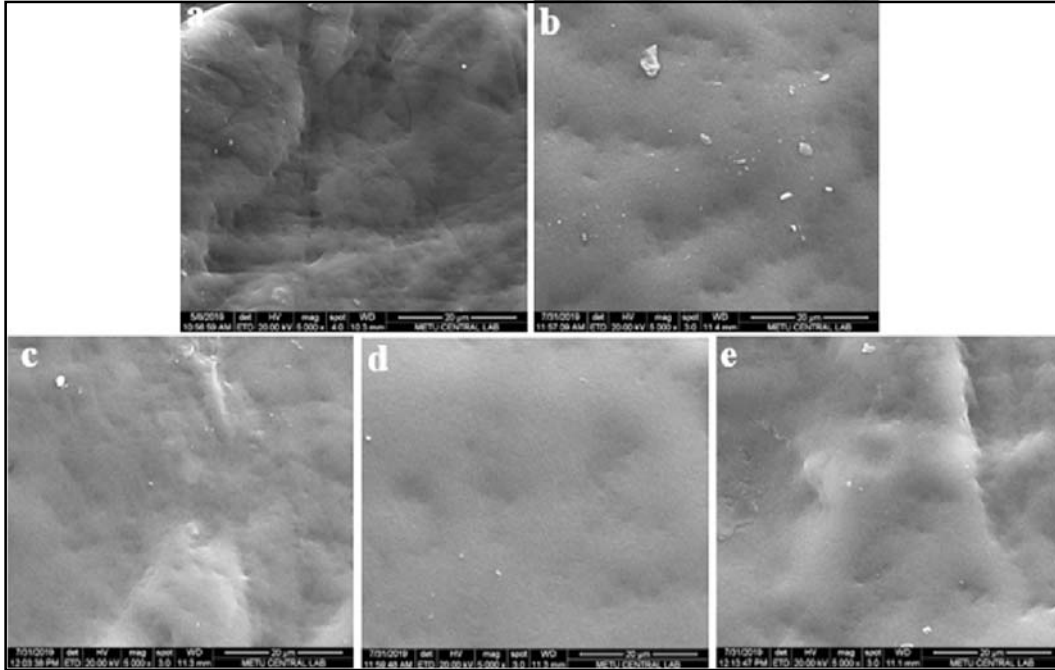


Fig. 6. SEM images (5000X) of a) PE b) 10CH c) 10GLY1 d) 10SOR1 e) 10PEG1 films

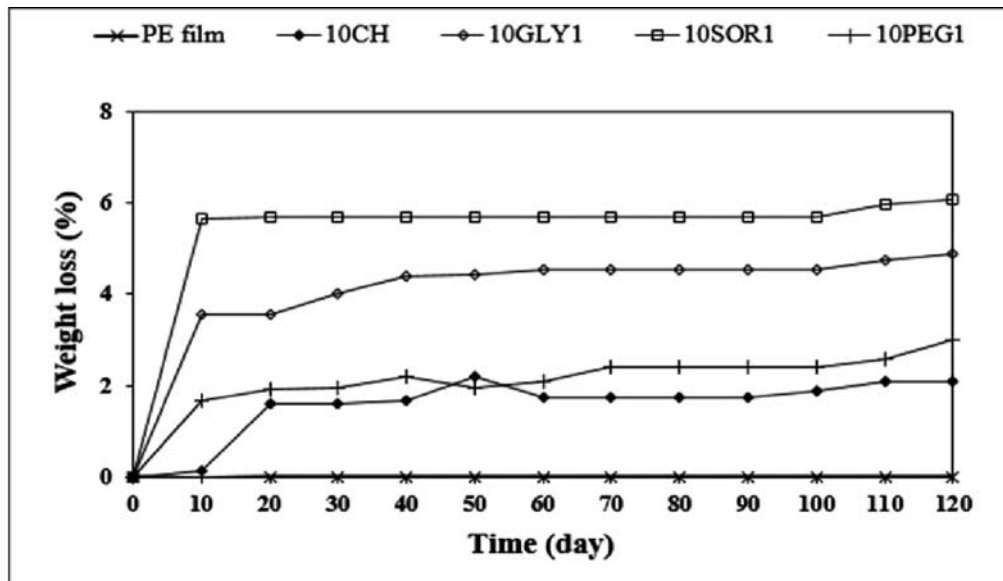


Fig. 7. The percentage weight loss of PE/CH films versus the number of days

of CH than tensile strength. The more extensible and thermal stable film was obtained with PEG among the films containing other plasticizers. Contact angle value of PE decreased with the addition of 10 wt.% of CH into PE. Although, contact angles of CH-PE films plasticized with PEG and SOR were similar, they exhibited higher value compared to CH-PE film plasticized with GLY. The best water vapor barrier property was observed on the film containing PEG compared to the films containing other plasticizers. The film containing SOR underwent biodegradation rate at a faster compared to the films containing other plasticizers. The blend films containing PEG and SOR could serve as an alternative packaging material to reduce environmental issues associated with synthetic packaging films. Further research should be focused on improving the properties of the PE/CH films with plasticizers at different ratios.

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