Effect of Chemical etching on Linear Low Density Polyethylene (LLDPE) /Chitosan blend film

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Abstract— Nowadays, waste natural polymer such as chitosan had created alternative material for food packaging as it is more safe and environmental friendly, cheap, biodegradation and have inherent biocompatibility properties. In this work, chitosan had been employed and blended with Linear Low Density Polyethylene (LLDPE) with different composition via twin screw extrusion. Chitosan having antimicrobial properties had to be sandwiched to optimize antimicrobial properties as too low antimicrobial activity earlier were found for blended chitosan/LLDPE film. Surface treatment of LLDPE via acid chemical etching technique were performed. Effect of film surface by chemical etching were examined through morphological SEM analysis. Structural feature was analyzed with FTIR and surface adhesion were found to be enhanced with higher chemical etching concentration.

Index Terms— Surface modification, Hydrophilicity, Adhesion, Chitosan, Chemical etching, Surface treatment, Biodegradation

1 INTRODUCTION

PACKAGING are widely used to store almost all food product that are available in market. The quality of packaging will influence the shelf life of food either coming from the growth of microorganisms that are present in air or from the food itself. The symptoms of product deterioration generally include off-flavor, the changes of the food colour and off-odour in the packaging. The reduction in food product shelf life were found to result from the influence intrinsic and extrinsic factors affecting the extent of the phenomena of sorption and migration process [1]. The intrinsic factors may include the quality of a food package which were influenced by the properties of the packaging material use. Some of the packaging materials used are plastics (mainly polyethylene PE and propylene PP, glass, pulp and papers. Plastics packaging are popular due to their low cost and low migration of water and inert to chemicals. [2][3][16] The extrinsic factor affecting food shelf life include mechanical stress, temperature, permeation of gases for example oxygen that pass through to the plastic film and vapor.

The use of packaging containing antimicrobial agents is more efficient and market demand since the antimicrobial agent (AM Agents) are migrating slowly from the packaging material to control and maintain the quality of food in the packaging. The increasing consumer health consciousness, increase demand on healthy food, preventing early onset of chronic diseases, and prolong the shelf life of food product are the main reason for the development food packaging film [4].

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Film need to prevent from the material migration into food and can control the quality of food product by retarding the growth of microorganism onto the food product.The packaging film was fabricated employing inorganic additive which impart antimicrobial properties which include silver oxide, zinc oxide, copper oxide and titanium dioxide[4]. But using these oxides, some critical issues faced include the material migration into food and will influence the food safety and health hazard [5]. The migration can be determined in two ways which are global migration and specific migration. The global migration means all compound were migrate into the food and specific migration means the transfer of known component. The regulations had specify the limit for both global and specific migration, thus it can give bad effect to our food safety and human health [6].

Chitosan is a natural antimicrobial agent and it is widely used in biomedical and food industries because of its high antimicrobial properties, high killing rate and lower toxicity [7]. In food application, the chitosan used were directly coated on the surface of fruits, eggs and meat products [8]. Moreover, chitosan were coated on paper for food packaging may enhance the gloss and the oxygen barrier properties of the paper [9]. However, there are limited studies on chitosan coated with polyethylene (PE) films [10] [11]. Polyethylene has long aliphatic hydrocarbon consisting carbon and hydrogen and PE is nonpolar. As a result, the PE were difficult used for applications that involving adhesion, hence adherence for lamination or coating need to be made for good lamination. Surface modification of the PE film in order to coat chitosan were required. Surface modifications onto PE surface need to be perform to

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create surface charges and ionized; some industries use established corona treatment or heat treatment to create surface polar charges for printing on the PE sheets [12] [13].

Effect of acid treatment will be use to perform surface modification of PE [14] [15]. PE were easily attack by oxidizing agents and subsequent heat treatment may further enhance the ioinisation or oxidation of PE surface. Chitosan coated PE were achieved by dipping or immersed in chitosan method. The steps involved are, PE blend film immerse into chitosan with acetic aicd solution followed by spreading the chitosan with acetic acid solution onto the PE blend surface and finally electrospraying chitosan onto polymeric surface [12]

TABLE 1
FORMULATION OF LLDPE AND CHITOSAN BLEND

Samples	Polyethylene (%)	Chitosan (%)	AM agent(%)
1	100	-	-
2	95	5	1
3	90	10	1
4	85	15	1
5	95	5	-
6	90	10	-
7	85	15	-

2 METHODOLOGY AND MATERIALS

The materials used in this study include Linear Low Density Polyethylene (LLDPE), chitosan with/without AM agent with composition 5%,10%, 15% of chitosan. LLDPE of grade LD0206 having MFI 0.26 g/10min from TITAN were employed as the base PE resin. Chitosan were supplied by Xi'an Wison Biological Technology Co., Ltd. Food grade with deacetylation purity of 95 %. Samples were formulated as in table 1and compounding performed were mixed with the ingredients as in Table 1 using twin screw extrusion with temperature barrel set at 145 ℃ to 150 ℃ and film blowing were performed via film blowing unit to produce plastic film for packaging and the temperature.

2.1 Testings

Testings were conducted for compounded LLDPE/Chitosan blend. The testings performed include Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

1. Fourier transforms infrared spectroscopy of chitosan and polyethylene films were carried out on a Perkin Elmer FTIR. This testing carried out in order to study the interaction between the functional group in chitosan based films and identify the comparison between sample before and after surface treatment method.
2. The morphology of the chitosan and polyethylene films was examined on their fractured surfaces before and after surface treatment and size of films about 1cm x 1cm were measured The samples of chitosan and polyethylene films were sputter coated with gold using a miscroscope sputter coater.

3 RESULTS AND DISCUSSION

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The Fourier Transform Infrared Spectroscopy (FTIR) test were carried out by blending the different percentage of chitosan and polyethylene with 1% of Antimicrobial AM agent. The purpose of this test is to determine the presence of functional group of chitosan, polyethylene and Antimicrobial AM agent .Below shows the comparisons between before and after surface modification by etching the film with concentrated sulfuric acid.

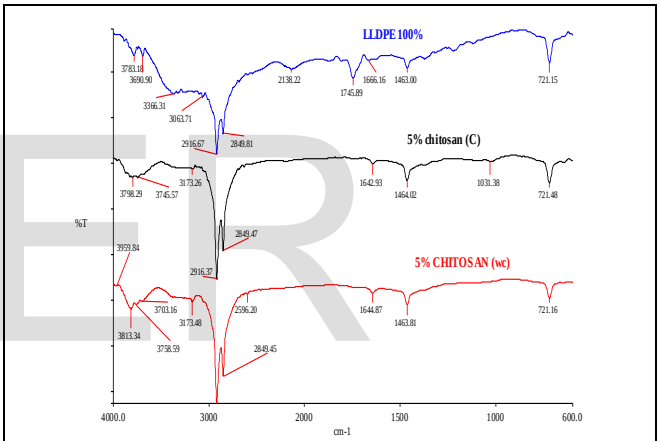

Fig. 1. The sample before surface modification

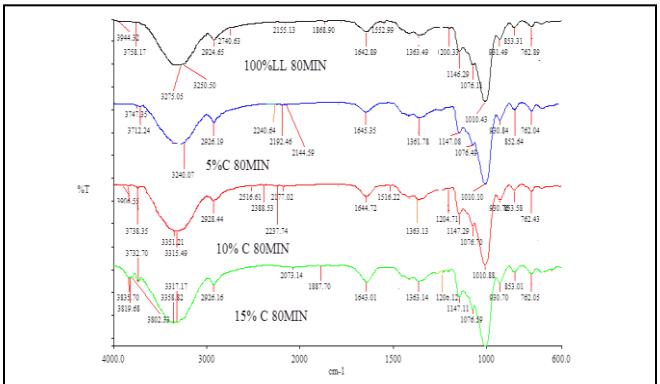

Fig. 2. The sample after surface modification due to 80min treatment

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Fig 1 show the sample before surface modification of film and Fig 2 and Fig 3 shows the FTIR spectra of LLDPE incorporated with different composition of chitosan and AM Agent before and after surface modification with different time of treatment. FTIR spectra of Chitosan shows, bands at 3000-3500 (NH bond)[3]. This band in the range of 3000 to 3500 are due to O-H and N-H stretching vibrations. Furthermore, the FTIR spectra of AM show bands at 1000 to 1320 correspond to C-O bonds [15]. The broad band in the range at 1000 to 1320 is due to C-O stretching vibrations. FTIR spectra analysis can identify the chemical change on the surface before and after acid treatment. From the result above, the fig. 2 after acid treatment showed the presence of new absorption bands between 1200-1250 cm-1 corresponding to C-O bonds which two represent ester group followed by 1800-1500 cm-1. These two absorptions had a lot of new polar groups generated during oxidative reactions. The new band are mainly assigned to group that containing carbonyl such s ketones, aldehydes, carboxylic acid and even some C=C bonds[17]. The absorption band from 760-660 were more intense at Fig 2 which are assigned as methylene group of each etched sample compared to Fig 1 before acid treatment.

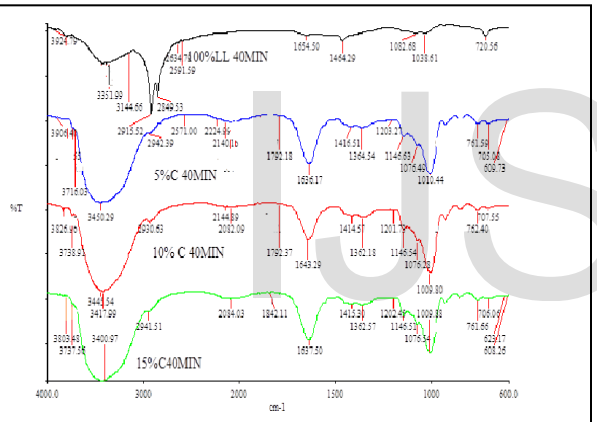


Fig. 3. The sample after surface modification due to 40min treatment

From the FTIR spectra above, it can be seen that characteristics peak of LLDPE, Chitosan and AM Agent were exhibited and confirmed to be present. The comparison of sample before and after etching can be identified by the new absorption bands. The intensity of the new absorption bands increase when the etching time increases.

3.2 SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron microscope (SEM) was used to observe the morphological surface of film before and after coating with chitosan. As a result, Fig 5 showed roughness surface presence compared to the control film (Fig 4) having smooth and continues structure. The roughness surface was found vigorously due to 15% of chitosan in the LLDPE matrix film. After etching time at 20min and coated with chitosan solution, at fig 6 resulted in less surface irregularities than fig 7. Trenches of surface were formed after long treatment process of40 min. The amorphous region of LLDPE films have loosen chain packing structure that may easily be etched by oxidative acids [18].

Fig. 7 shows the morphology of etched LLDPE/Chitosan blend film at 60min and coated with chitosan solution. It can be seen that the film surface contains spherical microparticles. When the treatment time increase from 20min to 1h for immersion film into concentrated sulfuric acid, chain scission and destruction of amorphous parts happen, the irregular and roughness surface increase with a bulky particle.

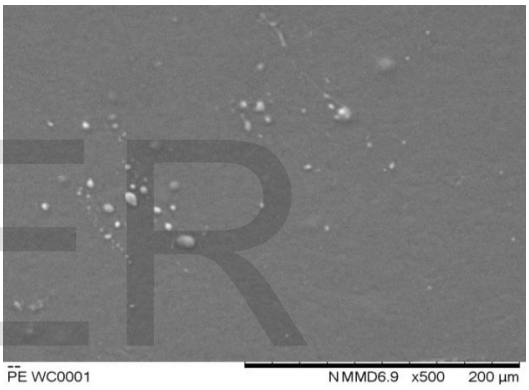


Fig. 4. Control sample (LLDPE) before treatment

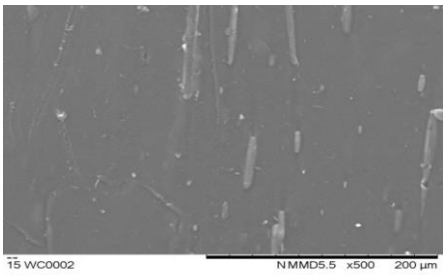
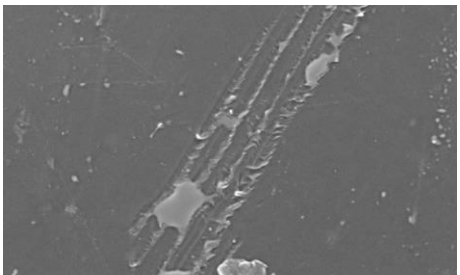


Fig. 5. LLDPE/Chitosan film before treatment



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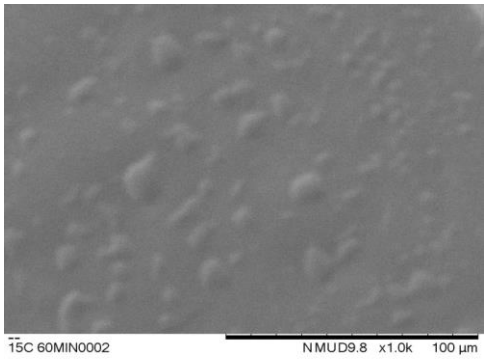

Fig. 7. LLDPE/Chitosan film after treatment and coated at 60min

4 Conclusion

The FTIR analysis depicted the presence of functional group of chitosan, LLDPE and AM Agent. After etching process, the new FTIR absorption bands between 1200-1250 cm^{-1} correspond to C-O bonds which represent ester group followed by 1500-1800 cm^{-1}. These band create new polar groups generated during oxidative reaction. From visualisation of the Scanning electron microscope, it indicated that when etching time increase, more destruction of amorphous parts occurred which had caused the higher surface roughness of film. The effect of acid by immersed in concentrated sulphuric acid is accompanied by oxidation process and surface roughness on PE. It introduce the new polar groups on the PE surface which are sulfonic groups are OSO, SO, SO3H and SOC. The intensity of induction new polar groups of PE surface is in direct proportionally to time of etching.

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References

[1] Ashish A Kadam, Thomas Karbowiak, (2015) Technique to measure sorption and migration between small molecules and packaging. A critical review. J sci Food Agric 2015;95: 1395-1407.

[2] Nurul-Akidah Mohd Yusak, Rahmah Mohamed, Muhammad Aizad Ramli. Mechanical Analyses of Polyethylene/Polypropylene Blend with Photo-degradant. Journal of Applied Science and Agriculture, 9(11) Special 2014,

[3] Rahmah Mohamed, Fatin Afiqah Juhari, Mohd Nurazzi Norizan. Bloom Characteristics And Strength Performance Of Biodegradable Pva/Sago Starch Blend With Two Different Plasticisers ; Green Building Technologies and Materials .Book 6 Vol. 3, 411-418pp

[4] Shin, G .;Lee,Y.H,; Lee, J.S.;Kim, Y.S.;Choi,W.S,; Park,H.j.j Agr Food Chem 2002,50, 4608-4614.

[5] Nurul-Akidah Mohd Yusak, Rahmah Mohamed, Muhammad Aizad Ramli. Mechanical Analyses of Polyethylene/Polypropylene Blend with Photo-degradant. Journal of Applied Science and Agriculture, 9(11) Special 2014,

[6] Bag DS, Ghosh SN, Maiti S (1998) Eur Polym J 34:855

[7] Chatterjee S, Adhya M, Guha AK, Chatterjee BP. 2005.Chitosan from Mucor rouxii: production and physico-chemical characterization. Process Biochem 40:395–400

[8] Jesús Guadalupe Pérez Flores , Judith Jaimez Ordaz , Javier Añorve Morga , Luis Guillermo González Olivares . .Araceli Castañeda Ovando, Elizabeth Contreras López Influence of Water Sorption Phenomena on the Shelf Life of Third Generation Snacks J. Food Process Engineering. 2017, Volume40, Issue1

[9] Duncan, T. V. (2014). Journal of Colloid and Interface Science Applications of nanotechnology in food packaging and food safety : Barrier materials , antimicrobials and sensors. Journal of Colloid And Interface Science, 363(1), 1–24.

[10] Dutta,P.K,; Dutta.J; Tripathi, V.S.J.Sci Ind Res 2004,63,20-31

[11] Siti Aishah, Rahmah Mohamed. Physical and mechanical properties of chitosan and polyethylene blend for food packaging film. International Journal of Mechanical and Production Engineering (2015), ISSN:2320-2092, Vol.3, Issues. 10.

[12] EU, Commission Regulation (EU) No 10/2011 of 14January 2011 on plastic materials and articles intended to come into contact with food(text with EEA relevance). Off J Eur Union L12/1:89(2011)

[13] Hsieh YL, Barrall G, Xu SQ (1992) Polymer 33:536

[14] Lee, C.H; A.n, D.H,; Park, H.J.; Lee, D.S Packaging Technology Sci 2013, 16, 99-106.

[15] Mohib Reza Kazimi, Iqbad Ahmed, Che Ku Mohammad Faizal. A short review of Hydrophilic surface modification methods for low density polyethylene; International Conference on chemical innovation (ICCI 2011), 23-24 MAY 2011, TATI University College,pp.203-206.J.

[16] Rahmah Mohamed, Fatin Afiqah Juhari, Mohd Nurazzi Norizan. Bloom Characteristics And Strength Performance Of Biodegradable Pva/Sago Starch Blend With Two Different Plasticisers ; Green Building Technologies and Materials .Book 6 Vol. 3, 411-418pp

[17] Suyatma NE, CopinetA, Tighzert L.Coma V. Mechanical and barrier properties of biodegradable films made from chitosan and polylactic blend. J p olym Environ 2004; 12(1);1-6

[18] Torres, A., Guarda, A., Moraga, N., Romero, J., & Galotto, M. J. (2012). Experimental and theoretical study of thermodynamics and transport properties of multilayer polymeric food packaging, 713–722