Thermal characterization of blown LLDPE/Chitosan blend film and Coated blend film

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Abstract—Waste natural polymer such as chitosan can be the future material in food packaging as it is biodegradable and have antimicrobial properties. In this work, melt compounding of Chitosan had been blended in this work with Linear Low Density Polyethylene (LLDPE) using twin screw compounder for use in film blown extrusion. Different composition of Chitosan and LLDPE were fabricated into films. Thermal characterization of chitosan/ LLDPE were performed with Differential Scanning Calorimeter (DSC) . Crystallinity of the films, their compatibility and melt temperature for each blends showed lower values with higher chitosan composition and Thermal Gravimetric .

Keywords: Surface modification, Hydrophilicity, Adhesion , Chitosan , Antimicrobial film

1 INTRODUCTION

Nowadays, packaging is an important product that used in food industry. The function of packaging is to protect the food from the external influence and damage the food product. This food packaging can be called as active packages that will extend the shelf life and enhance the quality and safety of food.[1] Besides that, the packaging are incorporated with additives such as antioxidant, antimicrobial, biocompatibility and biodegradable component which impart their functional properties. In this area, chitosan is selected to be the suitable organic waste material that can blend with linear low density polyethylene (LLDPE) as film because it has strong antimicrobial activity against gram-negative (Escherichia coli) interacting with long positively charged chitosan molecules causing distruption on the cell [2]. Films of biodegradable and degradable types had been used widely involving oxo , photo degradable additive types and blend of starch/PLA /PVOH type polymers [3-5] There are several factors that affect the antibacterial activity of chitosan which are molecular weight (MW) and concentration. The minimum inhibitory concentration (MIC) of chitosan ranged from 0.005 to 0.1% depending on the species bacteria and molecular weight of chitosan [6] and was varied depending on the pH of chitosan preparation [7]. Pure chitosan films are fragile and need plasticisers to reduce frictional force between the polymer chain, thus will improve the mechanical strength properties [8][9]. Plasticisers were used to overcome chitosan film brittleness, imparting chain flexibility to chitosan. Polyethylene glycol (PEG) are widely used as plasticizer in chitosan film. PEG were generally small molecules that intersperse and molecules are trapped between polymer chain, disrupting hydrogen bonding, which increase the flexibility, water vapor and gas permeability [10][11] In order to improve the weakness of chitosan film blending with PEG can assist further processing with synthetic materials such as PE which are investigated here. This research aimed to form chitosan blend with LLDPE and coat with thin chitosan layer on LLDPE films. LLDPE is largely use in flexible film packaging ; they are linear polyethylene with short chain brances. The crystallinity of LLDPE is higher than LDPE. LLDPE has excellent mechanical properties such as tear, impact strength and higher tensile strength .[12]

The combinations of chitosan and LLDPE for producing food packaging film can improve biodegradability of film as chitosan has inherent biodegradability characteristic. However, has hydrophilic character and LLDPE is hydrophobic character which may impose incompatibility,therefore, blend need to be modified using appropriate treatment methods especially whereupon another layer of film is to be coated. Non-polar group from LLDPE limits its use in some composite applications and coatings due to lack of adhesion and chemical treatment via, dielectric, acid immersion, corona treatment etc had been studied [1].Effect of coating layer and their thermal properties are being investigated in this study and upon immersion with acid of PE/chitosan blend.

There are several methods to improve the adhesion of LLDPE chain which are:

1.1 Dielectric barrier discharge (DBD) plasma

This method used to improve the surface wetting and adhesion properties. This speed operation needs minutes or second to reduce energy consumption. The process of plasma can generate radicals and excited species which are able to initiate chemical and physical modifications within depth of nanometers on the surface polymer [13]. Previous reported that the surface free energy and hydrophilicity of PE may improve after DBD plasma treatment and some oxidized species are presence on the surface.

1.2 Chemical etching

This technique involved chemical etching of polyolefin by nitric acid, sulphuric acid and chromic acid. Other than that, this technique was produce surface roughness and introduce polar group onto the surface polymer [14] [15]. There are several method used in chemical etching method which are electrospraying chitosan solution, immersion chitosan onto polymeric surface and spreading the chitosan solution onto the PE surface.

Chemical treatment via immersion of acid treatment at different time were demonstrated and PE/chitosan blend film were investigated for their thermal stability and transition

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temperatures.

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 blow-ing were performed via film blowing unit to produce plastic film for packaging and the temperature.

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	-

2.1 Testings

Thermogravimetric Analyzer was used to determine decomposition temperature, Td and percentage of weight loss between the effect of uncoated and coated surface according to ASTM E1131, Standard Test Method for Compositional Analysis by Thermogravimetry. The film was placed in sample holder and sample holder was then enclosed during test. Thermal stability of specimens has been studied by TGA in the range of 30-900^{o}C, with heating rate at 50 ^{o}C/min. In this test, specimen was uniformly heated and percentage of weight loss of specimen was taken.

Differential Scanning Calorimetry (DSC) test approximately 10 milligrams film from each composition were heated at controlled rate temperature according to ASTM Standard Test Method for Transition Temperature of Polymer by Differential Scanning Calorimetry (D 3418). DSC was performed used Perkin Elmer Differential Scanning Calorimetric Analyser at a temperature from 30.00°C to 200.00°C.

Heating and cooling rates were set at 10°C/min. DSC test method determines melting point (Tm), amount of energy which a sample absorbs while melting (Hm), crystallization point (Tc) and amount of energy that a sample would release while crystallizing (H*). Degree of crystallinity (Xc) values were evaluated as follows:

$$X_C(\%) = \frac{\Delta Hm}{\Delta H^* \text{ x } 100\%} \quad (1)$$

where Hm and H* are melting heats from fusion of composite and 100% crystalline LLDPE.

3 RESULTS AND DISCUSSION

The DSC curve of LLDPE/Chitosan blend film before and after coated process were analysed to determine differences in their thermal behavior. Figure below shows Tm, Tc and Δcp value of PE /Chitosan of different composition before treatment and coating process:

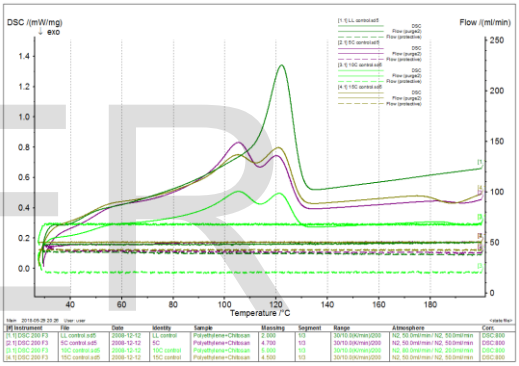

Fig. 1. DSC curve for LLDPE/Chitosan blend film before coated with chitosan solution

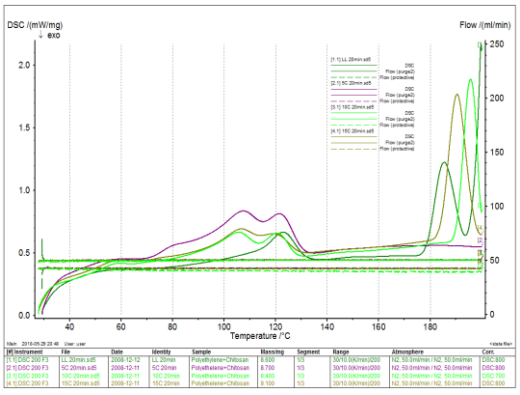

Fig. 2. DSC curve for LLDPE/Chitosan blend film after coated with chitosan solution

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Figure 1 refers to heating curve of the three formulated blends with chitosan and virgin PE before treatement and Figure 2 refers to treatment with chitosan solution. The DSC thermogram from Figure 2 shows significant endotherm peak formed around 185ºC to 200ºC which might refer to recrystallization of the chitosan peak. The high Tm of second peak is from the outer layer chitosan formed which did not undergo melt blending process.

Lower endotherm peak around 60ºC could be the low molecular weight PE and the antimoricabial agent AM used. Melt blending may have cause chain disruption during high temperature process and this could prevent realignment of chain. High second Tm peak pocesses after outerlayer coating had preserved the chitosan alignment of chain with amide strong linkage of chitosan polymeric network.

TABLE 2
THERMAL PROPERTIES OF CHITOSAN/PE BLEND BEFORE AND AFTER TREATMENT AND COATING PROCESS

Film	T_m (ºC)		T_c (ºC)		ΔH_m (J/g)		ΔH•(J/g)	X_c (%)	
	Before	After	Before	After	Before	After		Before	After
PE	127.2	-	122.2	-	105.63	-	293	36.05	-
PE/5%C	117.3	115.0	105.6	107.5	65.61	56.55	293	22.39	19.30
PE/10%C	117.1	114.6	105.5	105.6	45.93	33.55	293	15.67	11.45
PE/15%C	116.8	113.3	105.1	106.8	29.82	22.92	293	10.18	7.82

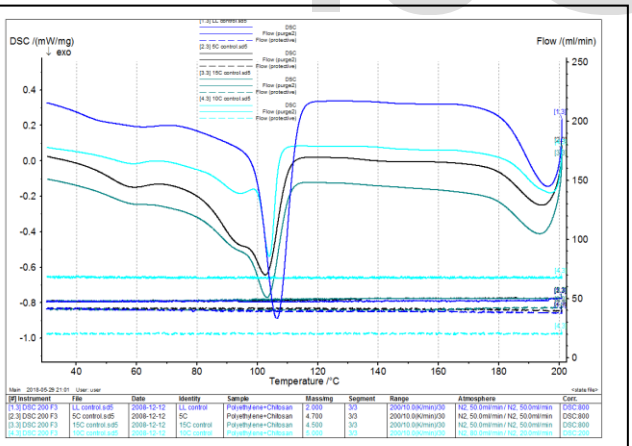

Fig. 3. DSC curve for cooling process before treatment and coating process for chitosan LLDPE blend film.

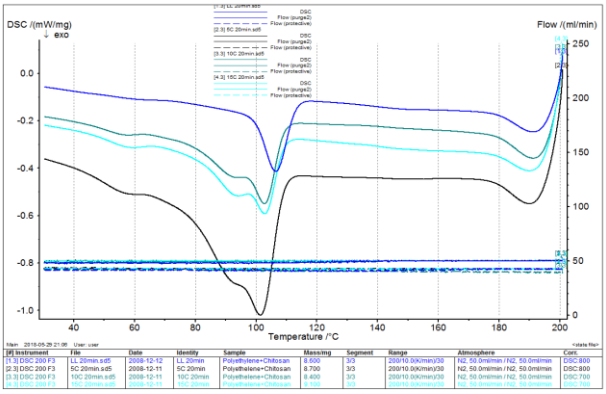

Fig. 4. DSC curve for cooling process after treatment and coating process for chitosan/LLDPE blend film

It was observed that both before and after treatment of coating process, thermogram has two peaks for blend with the peak of virgin PE. From the observation of Figure 1 and 2 , T_m value for virgin PE is 127.2ºC. From the peak, it can be seen that at PE/5%C is the highest T_m value before and after treatment and coating process compared to PE/5%C and PE/10%C blend which are 117.3ºC and 117.1ºC. There is a decrease in T_m for PE/Chitosan blend compared to virgin PE, which depicts the lower crystallinity of the PE upon incorporation of chitosan. The presence of chitosan particles in PE matrix may hinder the crystallization of virgin PE molecule, therefore disordering increase and crystallinity content have been reduced.

Overall, incorporation of chitosan had reduced the Tm of PE itself from 127ºC cto 116ºC. High endotherm of chitosan were visualised from outer layer chitosan formed from chitosan solution which is about 185ºC but both formed signifant crytallisation peak around 190ºC.

DSC cooling thermograms are shown in figure 3 and 4. It showed that the crystallization temperature of virgin PE is higher compared PE/Chitosan blend film around 115ºC to 117ºC. From the table 2 as stated, virgin PE films showed the percentage crystallinity is ~ 36.05%. As the chitosan composition increase from 5%,10% to 15%, the PE/Chitosan blend percentage crystallinity diminishes. Chitosan inhibits the close packing of the PE chain and reduce crystallinity[16] .According to Michael I., 2014, higher content of amorphous chitosan exists[8] Chitosan exhibited slower cooling process as the peak shift to the lower temperature about 105ºC. Cooling process via DSC had been performed by Rahmah et al. which depict blends of different polymers underwent lower crystallization [16]

4 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was also carried out in order to study the degradation of chitosan/LLDPE blend film before and after treatment/coating process. Thermal stability of chitosan/LLDPE film was measured using TGA as shown in Figure 5 and 6 below

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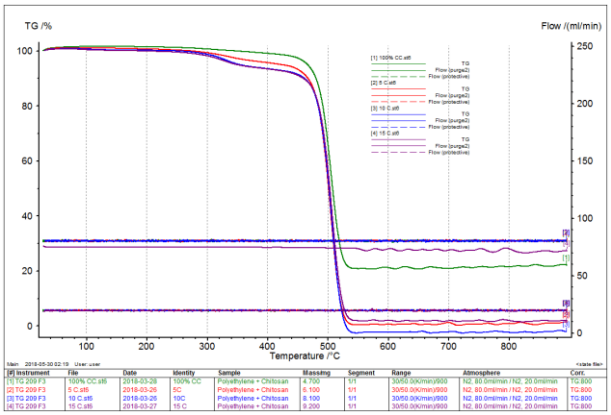

Fig. 5.TGA curve for control film

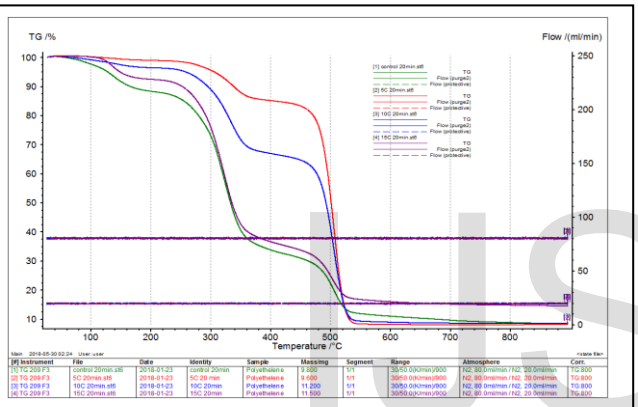

Fig. 6. TGA curve for chitosan/PE blend film after treatment and coating process

Figure 5 shows the weight loss and thermogram for PE/chitosan blend films as a function of temperature. Table 3 tabulated the thermal stability analysis before and after coating from TGA curve as in Figure 5.

Thermal stability of chitosan blend PE are lowered with increased in chitosan compositon. The virgin PE has lower Tmax decomposition as revealed from Table 3. Virgin PE showed maximum decomposition which occurs at 435°C ; lower than 2nd stage decomposition of PE chitosan blends which decomposed well above 500°C. PE chitosan blends showed two stages decomposition having first stage decomposition occurred at about 325°C to 330°C for 10 and 15% chitosan. For virgin PE, only one stage degradation profile shown but upon coating with chitosan, it had increased its temp of max decomposition to 480°C. Chitosan layer had increased the film thermal stability. For temperature of degradation at 10% for blends and virgin PE, it was found that highest chitosan composition of 15% did increase the thermal stability as the blend can maintain up to 90% sample around 493°C upon chitosan coating. Chitosan thermal stability, existence of amine group could prevent the degration of PE chain , intercept and retard the free radical formation upon high temperature. At higher compositon of chitosan , having higher amine group the thermal stability is less as excess amine is thought to assist further chain cleavage.

After treatment with chitosan coating, the 10% and 15% chitosan blend showed relatively no significant difference in thermal stability (have similar Tmax dec) . However, for 5% blend it exhibited increase first stage decomposition about 350°C and after treatment with chitosan coating, the decomposition depicted significantly dropped in thermal stability. This is because during treatment method, the sample film become more surface roughness and presence of new polar groups that easily break up and increase the thermal degradation of the sample.

The atomic force microscope (AFM) had been employed for relation between treatment time and surface roughness. It was found that the increase time of treatment had influenced the root mean square(RMS) value from 39.1µm (figure 7) to 41.0µm (figure 8) for PE/chitosan film surface. This result were related with physical or chemical removal molecules, chain scission and degradation process[17].

TABLE 2
THERMAL STABILITY OF CHITOSAN/PE BLEND BEFORE AND AFTER TREATMENT AND COATING PROCESS

Sample	Tmax (°C) Decomposition for 1st stage		Tmax (°C) Decomposition for 2nd stage		TGA Temperature at 10% Decomposition	
	Before	After treat/ coating	Before	After	Before	After
100%PE	-	-	435	480	479	162
PE/5%C	350	340	550	506	465	466
PE/10%C	330	330	507	507.5	460	461
PE/15%C	325	325	506	508	457	493

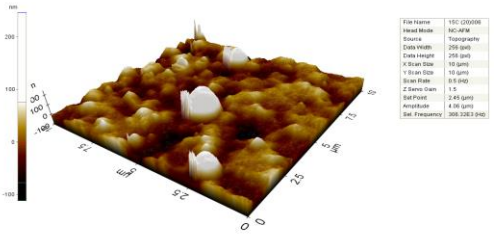

Fig. 7. Sample test before surface treatment method

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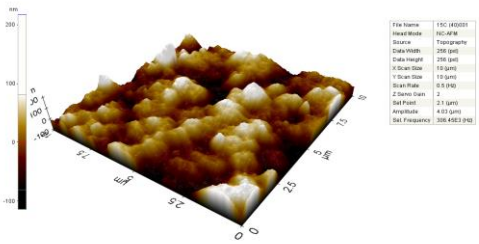

Fig. 8. Sample test after surface treatment method.

4 Conclusion

PE/Chitosan blend film showed two steps in thermal degradation with less degradation process and chain scission between the components of the polymer blends with increase chitosan composition. From DSC studies, two peaks formation showed that that PE matrix and chitosan phase are only partially miscible.Incorporation of chitosan had reduced the Tm of PE itself from 127°C to 116°C. High endotherm of chitosan were visualised from outerlayer chitosan formed from chitosan solution which is about 185°C but both formed signifant crytallisation peak around 190°C. The Tm of PE/chitosan around 116°C were slightly reduced upon higher chitosan incorporation from 5% to 15%, while enthalphies are also reduced signifying reduced crystallinity. Chitosan inhibits the close packing of the PE chain and reduced PE crystallinity.

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