



Research article

Effect of chitosan addition on the properties of low-density polyethylene blend as potential bioplastic

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ABSTRACT

Plastics based on low-density polyethylene (LDPE) blends generally have limited miscibility, and it is difficult to obtain a homogeneous blend. Although they show excellent properties, their thermal degradation rate is a concern. This work aims to realize a homogeneous blend with higher chitosan concentration, thus expected to increase its degradation properties. An extrusion technique successfully synthesized LDPE and chitosan blends. The mixtures were prepared by adding maleic anhydride (MA) and *tert*-butyl peroxybenzoate (TBPB) as a compatibilizer and initiator, respectively. The addition of MA and TBPB resulted in homogeneous blends and using chitosan concentration of 40 %wt resulted in better tensile strength and elongation at break. The water uptake increased along with chitosan concentration in the blends. The thermal behavior analysis of the blends conducted by simultaneous TG/DTA revealed that the increase of chitosan concentration tends to improve the blend's thermal degradation slightly. Moreover, chitosan addition resulted in approximately a hundred times larger biodegradability compared to plastics based on LDPE alone.

1. Introduction

Low-density polyethylene (LDPE) has been widely utilized for packaging materials because of its properties, including high gas permeability, high impact strength, and chemical resistance (Ferreira et al., 2005). It is also economical and is abundantly available; therefore, the production cost is low (Tharanathan, 2003). However, LDPE is a synthetic polymer and thus can result in environmental pollution. Several studies (Bonhomme et al., 2003; Vimala and Mathew, 2016; Restrepo-flórez et al., 2014) have shown that polyethylene-based polymers have a low biodegradation rate. Because of the interest in using LDPE in synthetic–natural blends, researchers have tried to tune its degradation rate behavior (Kim and Lee, 2002).

Many natural polymers exist as blend materials, such as starch, chitosan, and cellulose (Kim and Lee, 2002; Corre et al., 2010; Ermolovich and Makarevich, 2006; Shujun et al., 2005; Bourtoom and Chinnan, 2008; Timotius et al., 2019). Among these, chitosan is most attractive because of its excellent biodegradation properties. It has also been widely used in pharmaceutical utilization because of its

antibacterial and biocompatibility (Kammoun et al., 2013; Sunilkumar et al., 2012; Kusumastuti et al., 2017). A mixture of synthetic and natural materials exhibits different physical and mechanical properties in comparison to films with individual component. Also, the production process is relatively easy and inexpensive. Nowadays, it is still challenging to synthesize homogeneous synthetic–natural blends because they tend to be immiscible (Mir et al., 2011). The natural polymer usually has hydrophilic properties, while the synthetic polymer has hydrophobic properties. A compatibilizer is needed to ensure the homogeneous dispersion of nonpolar LDPE with polar chitosan in the blend matrix (Prasanna and Sailaja, 2010). Some researchers have proposed using a compatibilizer such as maleic anhydride (MA) to couple the immiscible binary mixture (Sunilkumar et al., 2012; Del Castillo-Castro, 2011; Quiroz-Castillo et al., 2014). The grafting reaction occurs between polyethylene chains, chitosan, and MA (Figure 1). In this process, an initiator is needed to promote radical polymerization. Previous studies have been conducted using *tert*-butyl peroxybenzoate (TBPB) as an initiator to accelerate the

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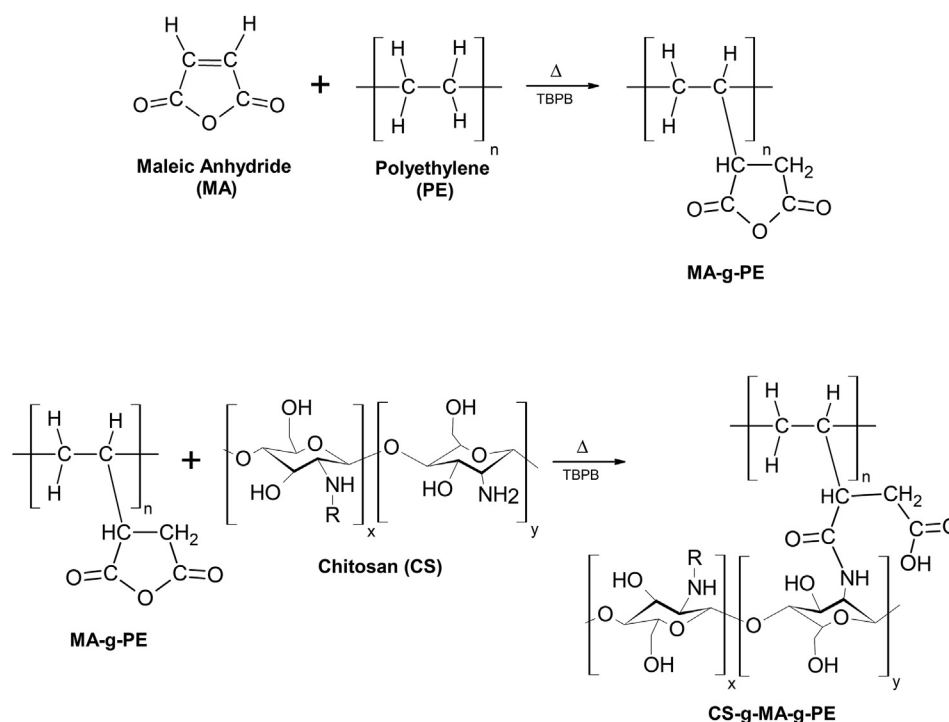


Figure 1. Scheme of reaction polyethylene-graft-maleic anhydride-graft-chitosan blend.

polymerization by producing radical chains (Chan et al., 2015; Zhou et al., 2017).

This present work aims to prepare and characterize a homogeneous LDPE-chitosan mixture by an extrusion technique with MA and TBPB as the compatibilizer and initiator, respectively. Quiroz-Castillo et al. (2014) synthesized an LDPE-chitosan film, which resulted in good processability and homogeneity with a chitosan concentration of 5–20 %wt. Martinez-Camaco et al. (2013) also synthesized an LDPE-chitosan blend using ethylene/acrylic acid as a co-polymer; they used a chitosan concentration of 5 %wt, as a higher concentration would not yield a homogenous mixture because of the immiscibility of the component materials. In contrast, the addition of a biodegradable polymer such as chitosan tends to increase the biodegradability of blended plastics. Therefore, our objective is to evaluate the addition of higher chitosan concentration in a homogeneous LDPE-chitosan blend, which improve the plastic biodegradability.

2. Experimental details

2.1. Materials

Chitosan powder with degree of deacetylation >90%, ash content <1.5%, protein content <0.5% and viscosity 10–500 cps was obtained from PT Biotech Surindo (Cirebon, Indonesia). Low-density polyethylene PFS 4020 was purchased from Petrochemia Plock, Poland. Maleic anhydride (MA) was supplied from Sigma Aldrich. TBPB was obtained from NOF Corporation, Tokyo, Japan.

2.2. LDPE-chitosan film preparation

The composite film was prepared in two steps; the chitosan and LDPE were mixed with a compatibilizer and initiator in a Labo Plastomill, and then the mixture was pressed.

First, LDPE pellets were added into a Labo Plastomill and heated at 160 °C to melt. Then, chitosan powder (10–40 %wt), MA (4 %wt/wt), and TBPB (0.25–1.0 %wt/wt) were simultaneously added. The mixing was performed under a constant temperature of 160 °C and speed of 50

rpm and lasted until all the materials were well homogenized. The concentration of chitosan, LDPE, and TBPB as the initiator was varied, as shown in Table 1. The percentage of MA and TBPB is based on the LDPE mass.

The LDPE and chitosan concentrations were calculated based on the LDPE-chitosan mixture's weight, while the TBPB and MA concentrations were determined by LDPE's weight. The melted composite from the Labo Plastomill was pressed using a hot presser under a pressure of 40 kgf/cm² to yield 0.5 mm of the composite film.

2.3. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy was performed to identify the existing of functional groups in blended polymer by characterizing its transmittance spectra. An FT-IR spectrometer (Shimadzu, Japan) was used for the measurements in a wavenumber range of 4000 - 400 cm⁻¹. All samples were prepared using KBr method.

2.4. Thermal analysis

Thermal analysis was performed by thermogravimetric and differential thermal analysis (TG/DTA Perkins Diamond Series) simultaneously. Approximately 5 mg of sample was analyzed and heated from room temperature to 420 °C with a heat rate of 10° C/min.

2.5. Mechanical analysis

The mechanical properties of all samples were characterized according to ASTM D882-02 standards. A universal testing machine (Gester K-01) was used for measurement for both tensile strength and Young's modulus. The average values were read based on the five specimens as a minimum tested sample for each composite.

2.6. Contact angle measurement

The hydrophilic properties of the LDPE-chitosan blend were analyzed by a contact angle goniometer DM-501 (Kyowa Interface Science, Japan).

Table 1. Composition of composite film.

Code	Chitosan (%wt)	LDPE (%wt)	MA (%wt/wt)	TBPB (%wt/wt)
A	-	100	-	-
B	10	90	4	1
C	20	80	4	1
D	30	70	4	1
E	40	60	4	1
F	30	70	4	0.5
G	30	70	4	0.25

Here 2 μ l of Milli-Q water was dropped on the blend surface with a microsyringe and monitored along 40 s of observation at room temperature.

2.7. Water sorption study

Water sorption analysis was conducted as described in previous studies (Sunilkumar et al., 2012; Aminabhavi and Harogopad, 1991; Nakhle and Wood-Adams, 2017). Samples were prepared with a rectangular shape of 2 cm \times 1 cm. After that, samples were immersed in distilled water. The excess water was regularly removed at a specific interval of time using a filter paper and then weighed immediately. The procedure was continuously repeated until a constant weight was obtained. The water sorption is represented as a mole % uptake (Q_t) determined from Eq. (1).

$$Q_t(\text{mole}\%) = \left[\frac{\left\{ \frac{\text{Mass of water sorbed by polymer}}{\text{MW of water}} \right\}}{\text{Initial mass of polymer}} \right] \times 100\% \quad (1)$$

2.8. Dynamic analysis of diffusion

The measurement of diffusion constant (D) is essential to determine the diffusion rate. The diffusion constant was calculated using Eq. (2) as described in a previous study (Nakhle and Wood-Adams, 2017). The diffusion process was considered as a double-sided diffusion through a plane sheet with a thickness of $2L$. In Eq. (2), each symbols, $M(t)$, M_∞ , and t are representing the water uptake (mole), saturated water uptake (mole), and time respectively.

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\left\{ \frac{D \cdot t}{4L^2} \right\} \pi^2 (2n+1)^2 \right] \quad (2)$$

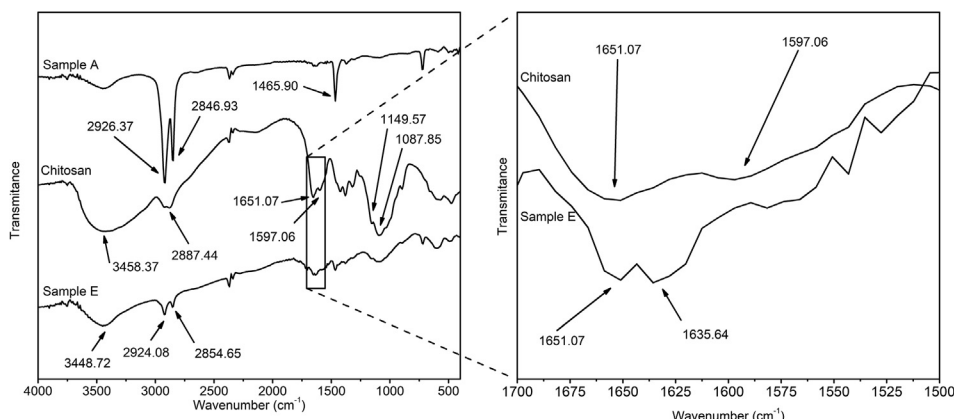


Figure 2. FTIR spectra of LDPE (sample A), chitosan, and LDPE-chitosan with 40 %wt chitosan (sample E).

2.9. Scanning electron microscopy

The blended polymer was sputter-coated using gold with VPS-020 Quick Coater (ULVAC KIKO, Ltd., Japan). The coated sample surface morphology was observed using a SEM Hitachi S-4800 (Tokyo, Japan) with a voltage of 15 kV and 300 times magnification.

2.10. Biodegradability study

Biodegradability study was conducted as described in the previous research with slight modification (Prasanna and Sailaja, 2012). Samples (2 cm \times 1 cm) were cut and then buried entirely in a depth of 10 cm inside a chamber contained soil with the humidity 40–45% at room temperature. After 80 days, samples were removed and washed gently, and then oven at 50 $^{\circ}$ C until the constant mass was obtained.

$$\text{Degradation}(\%) = \frac{(m_0 - m_t)}{m_0} \times 100\% \quad (3)$$

3. Results and discussion

3.1. Film preparation

In this research, a homogeneous film blend containing 10–40 %wt chitosan was synthesized using the proposed extrusion technique. The concentration of TBPB used in this study affected the film. It was not possible to use more than 1 %wt/wt of TBPB because it would result in poor homogeneity. For improving LDPE and chitosan blend's miscibility, the previous studies utilized 5 %wt/wt maleic anhydride as compatibilizer (Carrasco-Guigón et al., 2017; Quiroz-Castillo et al., 2014). However, in this research, by setting the lower proportion of maleic anhydride into 4 %wt/wt, the homogeneous blends were obtained.

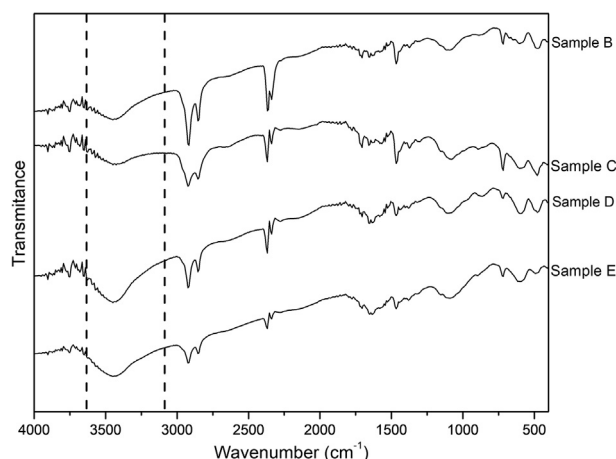


Figure 3. FTIR spectra of samples B (10 %wt chitosan), C (20 %wt chitosan), D (30 %wt chitosan), and E (40 %wt chitosan).

3.2. FT-IR spectroscopy

The spectra of sample A, chitosan, and sample E are presented in Figure 2. The peaks of the chitosan spectrum are similar to those of previous studies (Bourtoom and Chinnan, 2008; Sunilkumar et al., 2012). The band of chitosan at 3458 cm^{-1} was identified as the stretch of the OH and NH group, while the C–H bending region is shown at 2887 cm^{-1} . The band at 1597 cm^{-1} represents the N–H bending region of amide II, while the band at 1651 cm^{-1} is the C=O bending region of amide I and the band around 1149 represents the ether group in chitosan. While the spectra of sample A, peak at 2846, and 2926 cm^{-1} represented C–H stretching, while the peak at 1465 cm^{-1} represented the vibration of CH_2 . In the case for sample E with 40% of chitosan, the transmittance spectra show peaks at 2854 and 2924 cm^{-1} corresponding to C–H stretching, which is similar to pure LDPE band. Compare to the chitosan band, the shoulder peak of sample E around 3448 cm^{-1} shows more narrow than the chitosan band. The existence of chitosan in polyblend film can be shown by shifting of amide I into 1635 cm^{-1} . Thus, it confirmed that polyblend consists of both chitosan and LDPE.

The FTIR spectra of samples with different chitosan concentrations (Figure 3) show that the increase of chitosan concentration increased the transmittance of OH and NH bands (around 3450 cm^{-1}).

3.3. Thermal analysis

Simultaneous TG/DTA was used to characterize thermal properties and stability of blends (Villetti et al., 2002; Sunilkumar et al., 2012). The

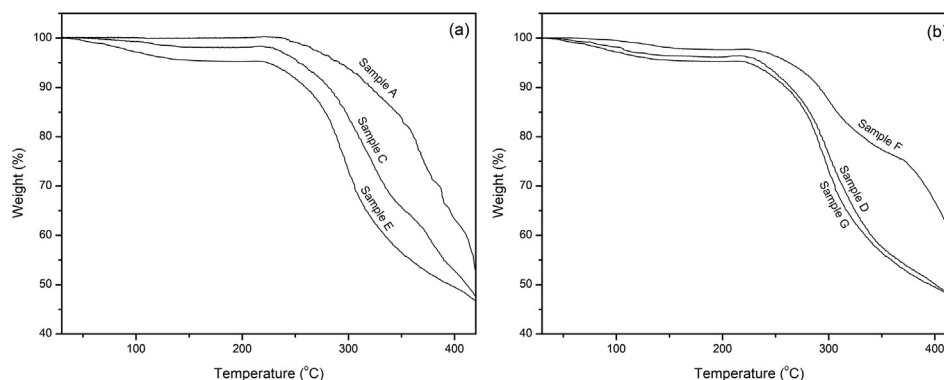


Figure 4. Weight loss of blends against temperature for (a) blends with the varied of chitosan concentration: sample A (LDPE), C (20 %wt chitosan), and E (40 %wt chitosan) and (b) blends with the varied of initiator concentrations: sample G (0.25 %wt/wt), sample F (0.5 %wt/wt) and sample D (1.0 %wt/wt).

thermal analysis showed the chitosan concentration effect on the thermal degradation of blends. Figure 4a shows the thermal degradation (%) of blends with various chitosan composition against temperature, and Figure 4b shows the thermal degradation of the blends with various initiator concentrations against temperature. The degradation stage of the LDPE and LDPE-chitosan blend corresponds with that of a previous study conducted by Prasanna and Sailaja (2012). Low-density polyethylene exhibited a single degradation step, whereas LDPE-chitosan exhibited two degradation steps. The first step occurred at a temperature below $120\text{ }^\circ\text{C}$ and was mainly due to the loss of water and other volatile materials. Higher chitosan contents resulted in a higher mass loss in this step. The second step was due to the thermal degradation of the polymer. Low-density polyethylene (sample A) began degrading at $240\text{ }^\circ\text{C}$, while sample C (20 %wt chitosan) and E (40 %wt/chitosan) started to degrade significantly at $230\text{ }^\circ\text{C}$ and $220\text{ }^\circ\text{C}$, respectively. The sharp degradation curve of the sample C and E compared to that of A (LDPE) is due to the degradation of chitosan component of the blends. The chitosan degradation involved dehydration, deacetylation, and chain scission. This indicates that increasing the chitosan concentration tends to slightly improve the blend thermal degradation. The polymerization was initiated by existing of organic peroxide as initiator such as *tert*-butyl peroxybenzoat (TBPB) which readily occurred homolytic to generate free radical. The addition of initiator concentration resulted in a significant increase in the degree of crosslinking, hence improve its thermal stability of blend. Even if the concentration of the initiator was as low (sample G), it resulted in low grafting efficiency. While at a high concentration of initiator (sample D), the grafted was achieved fastly and might inhibit some branches for additional grafting yielding for an almost constant degree of crosslinking.

Melting of plastic is a change into an amorphous liquid state from a solid crystalline state. There is no loss of mass, and no chemical change occurs, but it can be identified from the endothermic enthalpy change. The effect of chitosan concentration on the melting point (Figure 5) shows that sample A (LDPE) and blend samples B (10 %wt chitosan), C (20 %wt chitosan), D (30 %wt chitosan), and E (40 %wt chitosan) had melting points of 113, 110, 109, 109, and $108\text{ }^\circ\text{C}$, respectively. Compared to the LDPE film, the blend samples had a lower melting point. By increasing the concentration of chitosan, the melting point of the blends tends to decrease. This decrease in the melting point would reduce the energy consumption during manufacturing process, resulting in lower production costs; this indicates the feasibility of the proposed approach.

Plastics generally have limited miscibility, and it is challenging to find homogeneous blends. Interestingly, there is only one melting point peak for each blends sample curve, as shown in Figure 5. Thus, it can be concluded that the LDPE-chitosan blends were in a relatively homogeneous state.

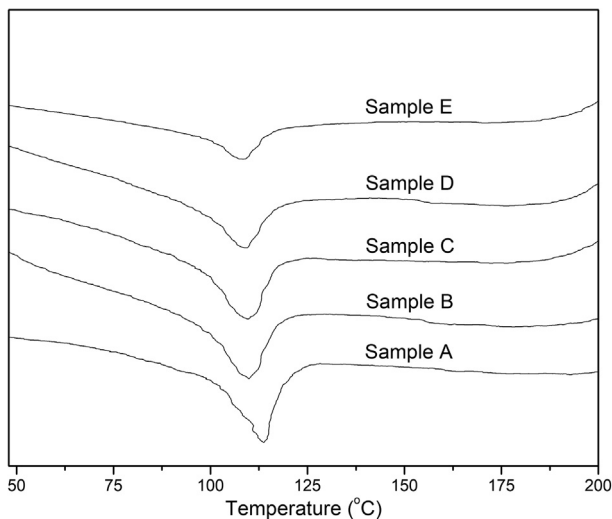


Figure 5. Melting points of sample A (LDPE) and blends B (10 %wt chitosan), C (20 %wt chitosan), D (30 %wt chitosan), and E (40 %wt chitosan).

3.4. Mechanical analysis

The effect of chitosan content on the mechanical strength of the homogenized samples was studied. With the increase of the chitosan content, both tensile strength and Young's modulus increased; however, the elongation decreased (Figure 6). This is because chitosan, as an immiscible component, has low ductility and is a rather brittle material; thus, its addition made the blend more rigid than pure LDPE film. In addition, the increasing tensile strength caused by the good interfacial adhesion between chitosan and LDPE matrix due to well dispersion of chitosan

particles (Sunilkumar et al., 2012). According to Sloan et al. (1986), both Young's modulus or elastic modulus and hardness are greatly influenced by the degree of crosslinking and also the uniform particles dispersion into the matrix. Quiroz-Castillo et al. (2014) synthesized LDPE/chitosan blends with a similar composition of chitosan content using glycerol as a plasticizer. By concerning the total amount of chitosan content in the blend, our results show better tensile strength on 10 %wt and 20 %wt of chitosan content. Reesha et al. (2015) suggested that the low tensile strength is resulted from an uneven dispersion of chitosan in the LDPE matrix. Thus, the homogeneity or evenly particle distribution of in the blended polymer is a key for increasing both tensile strength and Young's modulus.

In the present study, TBPB acts as an initiator to promote a radical reaction, and leads to generate chemical bonding in a blend, or cross-linking of LDPE-chitosan. The concentration of TBPB does not affect the tensile strength of the film (Figure 7a). Moreover, the result of elongation at break shows that there is an optimum value of TBPB, which obtained at 0.5 %wt/wt. This chemical bonding increases the tensile strength of the blend. Therefore, as the chitosan concentration increase, both tensile strength and Young's modulus are also increasing.

3.5. Hydrophilicity

The effect of chitosan and TBPB content on the water uptake (mole%) of the samples were studied. The water uptake increased with the chitosan concentration in the blends (Figure 8a); this is because chitosan is a hydrophilic polysaccharide with three predominant absorption sites: hydroxyl group, amino group, and the hydroxyl group or aldehyde group at the end of the polymer chain (Karjalainen et al., 2004). These absorption sites can promote water uptake, and thus improve the hydrophilicity of the blends.

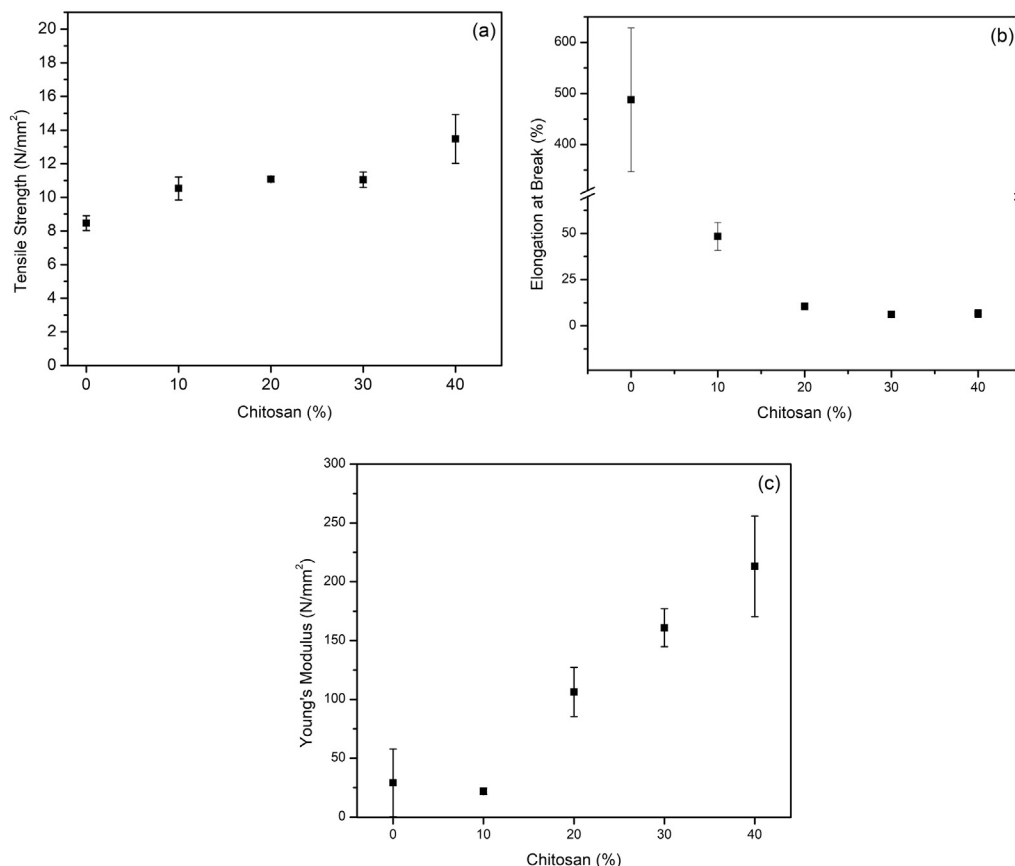


Figure 6. Mechanical strength of samples with different composition of chitosan including tensile strength (a), elongation at break (b), and Young's modulus (c).

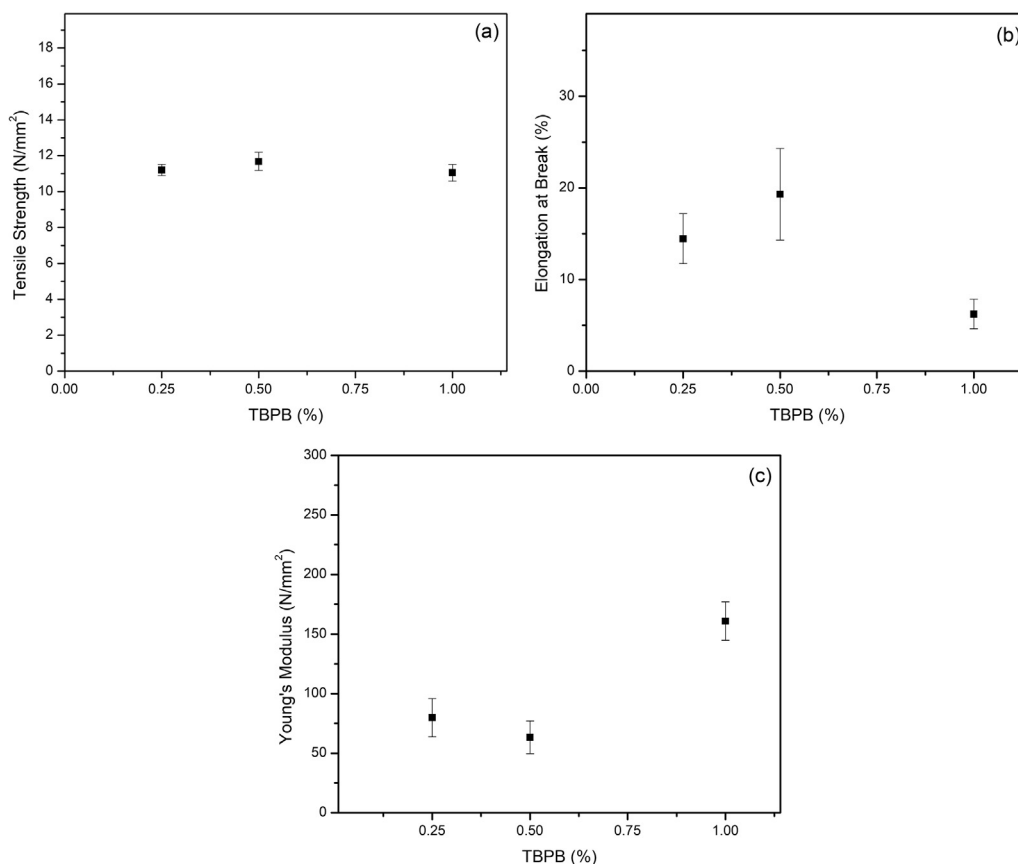


Figure 7. Mechanical strength of samples with different composition of TPBP at 30 %wt of chitosan including tensile strength (a), elongation at break (b), and Young's modulus (c).

On the other hand, the water uptake reduced with the increase of the TPBP concentration (Figure 8b); this might be due to the increasing amount of TPBP, which consequently produced more chemical bonding or crosslinking of LDPE-chitosan, and could reduce the predominant absorption sites.

The water uptake properties can affect the biodegradability. Chuayjuljit et al. (2009) explained that the high water uptake could improve the biodegradability properties of blend because the water absorption attracts microorganisms to attack, and they gain access to inside the matrix.

The effect of chitosan and TPBP concentrations on the diffusivity coefficient of the samples were investigated. The diffusivity coefficient was measured to determine the diffusion rate of a blend. Different

chitosan and TPBP content are not much affecting the diffusivity coefficient (Figure 9a and b).

The contact angle of samples C, D, and E were 105.3, 101.375, and 95.1 respectively. It means that the increase of chitosan concentration tends to reduce the contact angle.

3.6. Scanning electron microscopy

The surface morphology of blends with a variation of chitosan and initiator concentration was analyzed using scanning electron microscopy. All samples showed a smooth surface. The images (Figure 10) revealed that the distribution and dispersion of chitosan into LDPE blend was well mixed, thus resulted in homogeneous LDPE-chitosan blends. The existing.

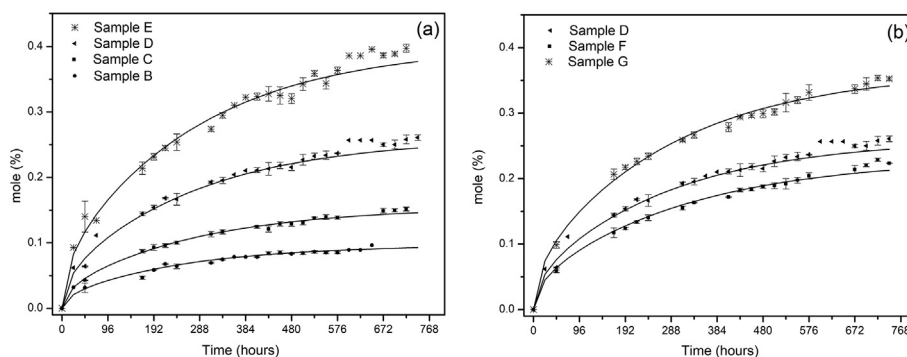


Figure 8. Variation of water uptake of samples with chitosan concentration (a) and TPBP concentration (b).

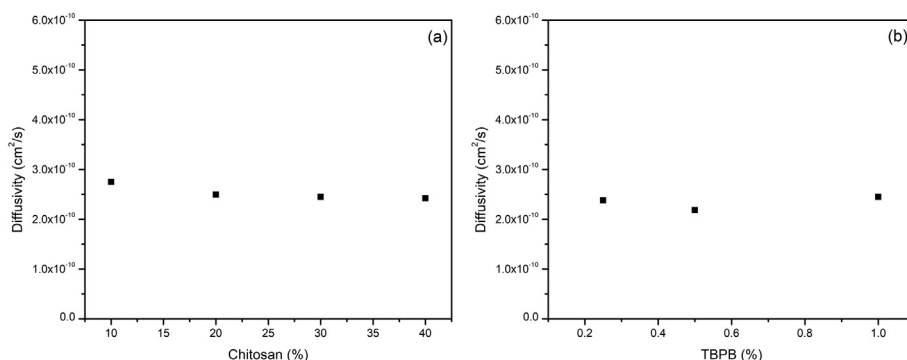


Figure 9. Variation of the diffusivity coefficient of the samples with chitosan concentration (a) and TBPB concentration (b).

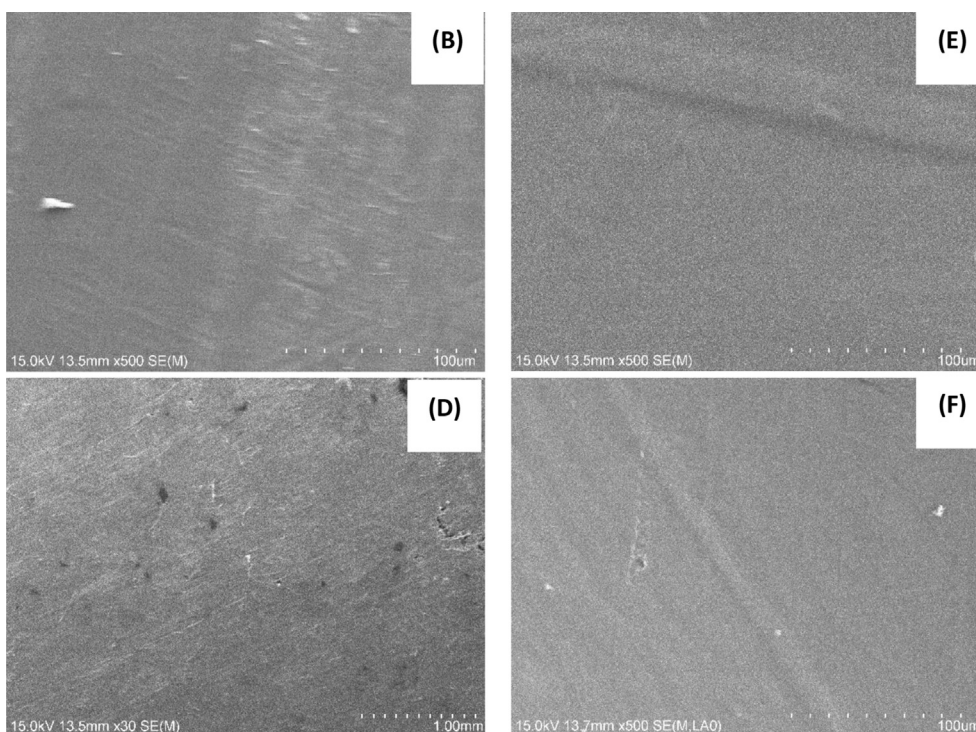


Figure 10. Morphology of the blends with a variation of chitosan concentration (B and E) and initiator concentration (D and F).

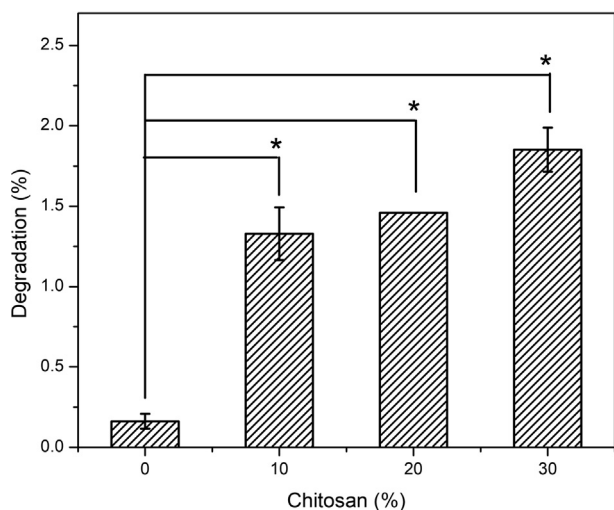


Figure 11. Biodegradation of the blends with variation of chitosan concentration.

3.7. Biodegradability study

Figure 11 shows the preliminary biodegradability study of LDPE-chitosan blends with various concentration of chitosan to calculate the percentage weight loss of films during 80 days burial. Although only a small amount of materials were degraded, the significant difference in weight loss percentage can be observed for pure and LDPE-chitosan with 30 %wt of chitosan. Prasanna and Sailaja (2011) explained the degradation of LDPE-chitosan might be triggered by the existence of chitosan as a nutrient source for microbial growth. Figure 11 shows that a higher concentration of chitosan causes an increase in the degradation rate. The obtained data were similar to the previous experiment conducted by Sunilkumar et al. (2012). The weight loss of LDPE-chitosan (triggered by *A niger* colony) increased along with the addition of chitosan concentration to 25 %wt. The addition of chitosan tends to increase the hydrophilicity and then promote the water uptake. The low degradation rate might also be caused by the character of LDPE. Sunilkumar et al. (2012) also described the microbial resistance behavior with existing of LDPE, hence no fungi growth on the LDPE surface. The degradation step of the synthetic-natural blend is initiated by destruction of the natural

compounds. Then, it leads to the appearance of crack propagation followed by the formation of free radicals on the surface of materials (Rogovina et al., 2018). Therefore in this case, the degradation step is initiated by the destruction of chitosan. In the following days of soil burial, it might be the chitosan which degraded the most.

4. Conclusions

A homogeneous blend of LDPE-chitosan containing up to 40 %wt chitosan was synthesized using MA and TBPB as compatibilizer and initiator via extrusion technique, respectively. The LDPE-chitosan blend exhibited a good tensile strength, which can be caused by the favorable interfacial adhesion between LDPE and chitosan. The addition of chitosan concentration led to an increase in water uptake, tensile strength, and Young's modulus and a decrease in elongation. The thermal study revealed that the blends melting point decreased with an increase of chitosan concentration. It will reduce energy demand during the manufacturing process, thereby reducing production costs. In conclusion, the chitosan addition in LDPE-chitosan blends profoundly influences the performance of the blends as bioplastics, mainly by controlling their mechanical properties and its degradability.

Declarations

Author contribution statement

Yuni Kusumastuti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Nur Rofiqoh Eviana Putri and Daniel Timotius: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Muh. Wahyu Syabani: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Rochmadi: Conceived and designed the experiments; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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