

THE PREPARATION AND BIODEGRADATION OF POLYBLEND PLASTIC FILM LOW-DENSITY POLYETHYLENE WITH PCL OBTAINED USING BIS(DIBENZOYLMETHANE)ZIRCONIUM(IV) CATALYST

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ABSTRACT

Low-Density Polyethylene (LDPE) is a type of synthetic polymer that is non-biodegradable and difficult to decompose by microorganisms. One solution to overcome this problem is to mix LDPE with a biodegradable polymer such as poly(ϵ -caprolactone) (PCL). The aim of this present study was to obtain an LDPE/PCL polyblend that can decompose in nature. The PCL used in this study was obtained from ROP ϵ -CL using a bis(dibenzoylmethanato)zirconium(IV) chloride catalyst. In this research, LDPE and PCL were mixed by the solvent casting method. While the solvent used is xylene. After that, the compatibility test, thermal properties test, and biodegradation test were carried out. Furthermore, the results of the biodegradation test showed that the LDPE/PCL polyblend produced could be degraded in the soil at a degradation rate of 3% for 60 days.

Keywords: Low-Density Polyethylene (LDPE), Poly(E-Caprolactone) (PCL), Bis(Dibenzoylmethanato)Zirconium(IV) Chloride Catalyst, Polyblend, Biodegradable.

RASĀYAN J. Chem., Vol. 15, No.3, 2022

INTRODUCTION

Petroleum-based polymer products are one of the polymers that are still dominant in the world market because they have various advantages, such as mechanical, thermal, and flexibility in several applications. Synthetic polymers are also designed to be resistant to environmental degradation. However, its nonbiodegradable characteristics and good durability lead to serious environmental problems. As a result, there is an accumulation of polymer waste which can contaminate the soil.³ Therefore, in the last few decades, researchers have conducted several studies on polymers that are environmentally friendly, especially for use as packaging. Researchers are also looking for solutions to minimize the problem of the accumulation of plastic waste so that it can decompose in nature.⁴⁻⁸ In nature, polymers undergo gradual decomposition due to the influence of various factors, such as light (photodegradation), humidity, air, temperature, wind (mechanical degradation), and macro or microorganisms (biodegradation). But the degradation of the polymer remains slow due to its good durability. Therefore, research on new polymer systems needs to be carried out to obtain biodegradable polymers. Nowadays, some synthetic polymers with biodegradable properties have been developed. For instance, aliphatic polyester poly(lactic acid) (PLA)², poly(ϵ -caprolactone) (PCL)⁹⁻¹³, poly- β -(hydroxybutyrate) (PHB), and poly- β -(hydroxybutyrate-co- β -valerate) (PHB-V).¹⁴ One type of polymer that decomposes very slowly in nature is polyethylene (PE). PE is often used in various applications because of its flexible nature, relatively cheap price, high strength, lightweight, water resistance, and good stability.¹⁰ Furthermore, PE is also widely used as ground wall insulation for medium to high power voltages. On the other hand, LDPE which is a type of PE has also been widely used in the electrical field, especially as cable insulation because of its relatively low permittivity and is difficult to recycle.¹⁵⁻¹⁶ In addition, another application of LDPE is as a packaging material, including food packaging, snack packaging, and beverage bottles.¹⁰

One of the popular methods for accelerating the decomposition of LDPE is by blending LDPE with a biodegradable polymer such as PCL. This method is cheaper than other methods, such as copolymer synthesis and polymer synthesis from natural sources.¹⁷ PCL can be produced through the ring-opening

polymerization (ROP) method using a zirconium complex catalyst.¹⁸ Other catalysts that have been used in the ε -CL polymerization are distannoxane¹⁹ and the complex of zinc.²⁰ But unlike the zirconium complex, these catalysts have the disadvantage of being susceptible to water and air vapor. Their Lewis acidity is also difficult to control, corrosive, and unsuitable for use in tropical climates. Previously, several researchers have conducted research on PE/PCL polyblends by varying the composition between PE and PCL. The choice of PCL as a degraded polymer is due to its good properties and it is compatible with various other materials, such as LDPE. This mixing will cover each other's weaknesses between PE and PCL. The resulting polyblend has better physical, mechanical, and thermal properties. In addition, the polyblend is also easily decomposed in nature, so it will be able to reduce the total amount of polymer waste in nature. The PCL used by previous researchers is a commercial material.²¹⁻²² The objective of this study was to produce LDPE/PCL polyblend plastic films that have better physical, mechanical, and thermal properties than pure LDPE and PCL. The LDPE/PCL polyblend plastic that is made is also supposed to be easy to break down in nature so that it doesn't pollute the environment. In this study, the PCL used was obtained from the ε -CL polymerization reaction using a bis (dibenzoyl methane) zirconium(IV) chloride [bis(dbzm)₂Zr] catalyst. This catalyst is suitable for use in tropical climates because it is not sensitive to water vapor and air.

EXPERIMENTAL

Materials and Method

The synthesis of complex catalyst, ROP of ε -CL, and polyblend LDPE with PCL were carried out at the Chemical Research Laboratory Universitas Negeri Medan. The materials used such as zirconium tetrachloride, ε -CL, and dibenzoyl methane ligands were obtained from Merck. LDPE is obtained from Petlin (Malaysia) Sdn Bhd. Meanwhile, PCL was obtained from the ROP of ε -CL using a bis (dbzm)₂Zr catalyst.¹⁸ Subsequently, characterization of LDPE/PCL polyblend was carried out using tensile strength test, FTIR, XRD, DSC, and SEM. These tools have the same specifications as we have reported in the previous report.¹⁸

Preparation of Polyblend Plastic Film

PCL components in the LDPE/PCL polyblend consisted of: 0%, 10%, 20%, 30%, and 40%. LDPE and PCL were each dissolved in the xylene solvent. The mixing was carried out at 120°C and 300 rpm for 3 hours using the reflux method. The next step is cooling the polyblend at a temperature of 100°C or below so that the xylene solvent evaporates and a polyblend film specimen is formed. After the two polyblend components are mixed and homogeneous, the mixture is then printed based on the size of ASTM D638. The polyblend obtained was determined using tensile strength test, FTIR, XRD, DSC, SEM, and biodegradation tests on waste soil located at Universitas Negeri Medan.²¹

Biodegradation of Polyblend Plastic Film

The biodegradation test begins by weighing the LDPE/PCL polyblend specimen to be planted using an analytical balance. Then, the specimens are buried in waste soil. Every 10 days, specimens are taken and sterilized using distilled water and 70% alcohol for 5 minutes each. After that, the polyblend dried and weighed. The rate of degradation of the burial in the soil was measured by observing changes in the weight of the specimen for 60 days.²³ On the other hand, the biodegradation rate of pure LDPE was also measured to compare with the biodegradation yield of polyblend LDPE/PCL.

RESULTS AND DISCUSSION

Plastic film is obtained by blending LDPE with PCL. PCL components were added in order to obtain a plastic film that has natural biodegradability but still has strong physical and mechanical properties like LDPE.²⁴ Additionally, the resulting polyblend is also expected to have high thermal resistance.

Tensile Strength Test

In general, the tensile strength test aims to determine the mechanical properties of a polymer such as tensile strength and strain. The tensile strength and elongation test of the LDPE/PCL polyblend is an important factor in determining the mechanical properties of a polymer. The testing standard used is the American

Society for Testing Materials (ASTM) D638. The results of the tensile and elongation tests with different composition variations are shown in Fig.-1.

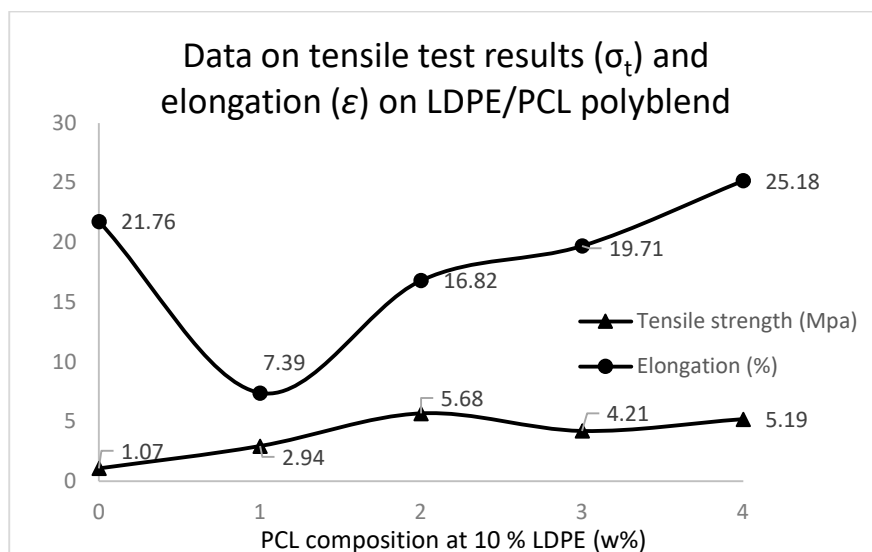


Fig.-1: Data on Tensile Test Results (σ_t) and Elongation (ϵ) on LDPE/PCL Polyblend

The mixing of LDPE with PCL produces more compatible polyblends than pure LDPE as shown in Fig-1. Plastic film made from a mixture of LDPE/PCL consists of 5 ratios, namely 10/0; 10/1; 10/2; 10/3; and 10/4. The optimum mechanical properties of the LDPE/PCL polyblend were obtained at a ratio of 10/4 with a tensile strength value of 5.19 MPa and a maximum elongation of 25.18%. Whereas, the tensile strength of pure LDPE (10/0) is only 1.07 MPa with an elongation of 21.76%. Generally, the tensile strength of the resulting polyblend is higher than that of pure LDPE. According to the tensile and elongation test results, at the ratio of LDPE/PCL 10/1 and 10/2, the tensile strength of the specimen increased. Whereas, at the ratio of LDPE/PCL 10/3, the tensile strength of the specimen decreased. Furthermore, at a ratio of 10/4, the tensile strength of the specimen increases again. On the other hand, the elongation value of the plastic specimens increased with the addition of the PCL composition. However, there was a decrease in elongation at a ratio of 10/1. This is probably due to the uneven level of homogeneity of the mixture so that the Van der Waals bond formed also weakens.³ The addition of PCL to polyblend is an important factor in producing an optimum mixture composition. The resulting polyblend will have better physical and mechanical properties than pure LDPE. This is because a Van der Waals bond has formed between LDPE and PCL. As a result, a physical interaction between LDPE and PCL is also formed. In addition, PCL has also filled the space on the LDPE surface. This is in accordance with the results of previous studies, that PCL has high biocompatibility and good mechanical properties.¹⁸

FTIR Spectrum Analysis

FTIR analysis was carried out to determine the absorption of functional groups of LDPE and PCL components on polyblend specimens. Through this analysis, it can also be known whether the formed polyblends have interacted physically or chemically. The spectrum of the results of the FT – IR polyblend analysis can be seen in Fig.-2 below.

The FTIR spectra of LDPE showed absorption at 2916 cm^{-1} and 2851 cm^{-1} , which corresponded to C–H stretching. The absorption at 1461 cm^{-1} corresponds to $-\text{CH}_3$ stretching, at 716 cm^{-1} corresponds to the $-\text{CH}_2$ bond in the vinyl group ($-\text{CH}_2-$).⁴⁻¹⁰ Whereas, the FTIR spectra of the LDPE/PCL polyblend also showed absorption bands at 2919 cm^{-1} , 2854 cm^{-1} , 1468 cm^{-1} , and 717 cm^{-1} . This absorption band has almost the same characteristics as LDPE. However, the absorbance intensity is slightly different. Next, the FTIR spectra of the polyblend also showed an absorption at 1717 cm^{-1} which corresponded to the C=O group. This peak is a typical peak of PCL which is supported by the presence of C–O and C–O–C absorption at 1179 , and 1223 cm^{-1} .¹⁰

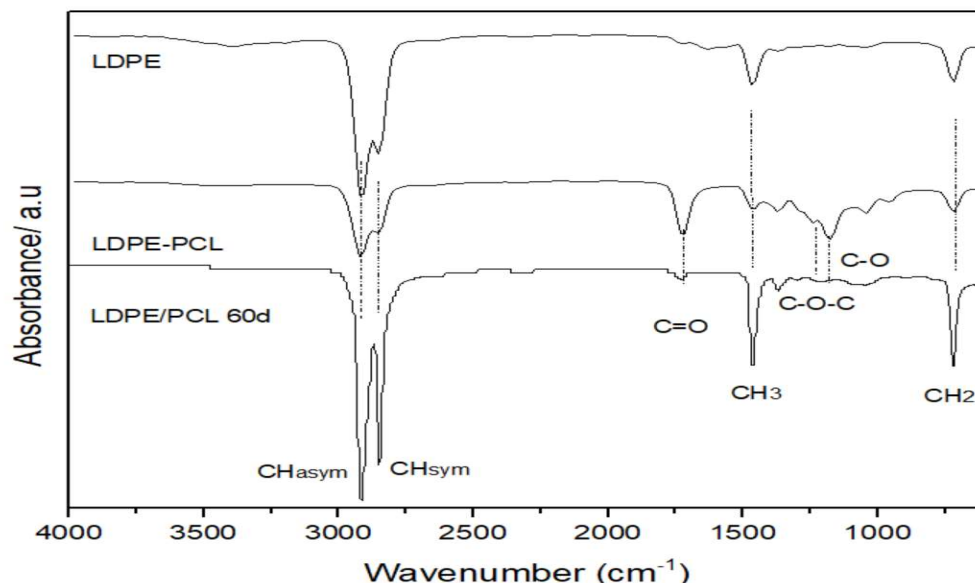


Fig.-2: FT-IR Spectrum of LDPE, LDPE/PCL, and LDPE/PCL after Biodegradation 60 Days

On the other hand, the biodegraded LDPE/PCL polyblends (for 60 days) were also analyzed using the FTIR spectrum. Both the LDPE/PCL polyblend and the biodegraded polyblend showed almost the same absorption. The difference is only in the absorption of C=O and C-O-C which weakens after biodegradation, which is in the range of 1717 cm^{-1} and 1179 to 1223 cm^{-1} . This phenomenon indicates that there has been a degradation of the LDPE/PCL polyblend. Usually, the biodegradation process starts from the PCL matrix so that oxygen is diffused into the polyblend, which then triggers the biodegradation process.¹¹ Based on the FTIR analysis, it can be seen that the LDPE/PCL polyblends have interacted physically. This is indicated by the absence of absorption of new functional groups outside the LDPE and PCL functional groups.

X-Ray Diffraction (XRD) Analysis

XRD analysis aims to determine the crystallinity of a polymer.²⁵ In general, polymers are semicrystalline, which means they have an amorphous part and a crystalline part. Then, LDPE, PCL, and LDPE/PCL polyblend are also semicrystalline polymers. Crystalline polymer XRD diffractograms tend to produce sharp peaks. In contrast, amorphous polymers tend to produce broad peaks. Then, the amorphous part and the crystalline part will show a specific scattering intensity. XRD diffractograms of LDPE, PCL, and LDPE/PCL polyblend are presented in Fig.-3 below.

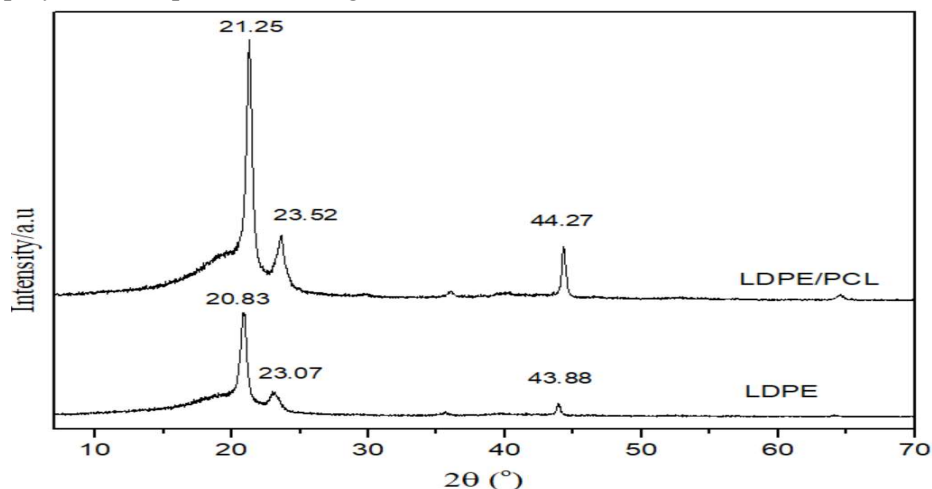


Fig.-3: XRD Diffractograms of LDPE/PCL Polyblend

The XRD polyblend diffractogram in Fig.-3 shows that there has been a change in the shape of the crystalline peak in the LDPE/PCL polyblend compared to pure LDPE. The crystalline peaks of LDPE were identified at $2\theta = 20.83^\circ$, 23.07° , and 43.88° . Whereas, PCL crystal peaks have been reported by our research group as identified at $2\theta = 21^\circ$, 22° , and 23° .¹⁸ Meanwhile, the crystalline peaks of LDPE/PCL polyblends were identified at $2\theta = 21.25^\circ$, 23.52° , and 44.27° . On the other hand, the highest crystal peaks of LDPE, PCL, and LDPE/PCL polyblends are presented in Table-1. According to that data, the degree of the crystallinity polymer is directly proportional to the intensity of the crystal peaks. Therefore, the order of the crystallinity from highest to lowest is PCL, polyblend LDPE/PCL, and LDPE.²⁶⁻²⁷ Generally, the addition of PCL to the polyblend has been able to increase the crystallinity of the polyblend compared to pure LDPE.

Table-1: Crystalline Peaks Intensity of Polyblend

No	Sample	2θ	Crystalline peaks intensity
1	PCL ¹⁸	21°	4806
2	LDPE/PCL	21.25°	2796
3	LDPE	20.83°	1141

Differential Scanning Calorimetry (DSC) Analysis

DSC analysis is widely used to determine the thermal transition of polymeric materials. This analysis aims to detect the thermal effects that accompany chemical and physical changes in the heated material. The heating rate during the DSC analysis was kept constant. Then, the generated data from this analysis are the melting temperature (T_m) and the decomposition temperature (T_d). The results of the DSC LDPE and LDPE/PCL polyblend tests are presented in Fig.-4.

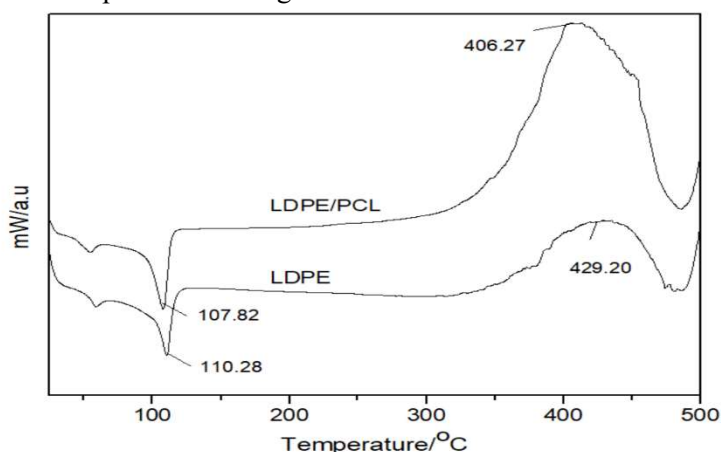


Fig.-4: The DSC Curves of LDPE and LDPE/PCL Polyblend

In Fig.-4, the melting points (T_m) of LDPE and LDPE/PCL polyblends are shown at 110.28 C and 107.82 C, respectively.²⁷ Meanwhile, the decomposition temperatures of LDPE and LDPE/PCL polyblend were 429.2 °C, and 406.27 °C. On the other hand, the enthalpies of LDPE and LDPE/PCL polyblend are 62.70 J/g and 57.78 J/g, respectively. In addition, PCL has also been analyzed by DSC as we reported in the previous work. As a result, PCL has a melting point, decomposition temperature, and enthalpy of 59.62 °C, 428.08 °C, and 109.00 J/g.¹⁸ The thermal properties obtained by the LDPE/PCL polyblend in this study were different from those of LDPE and PCL. Hence, these thermal properties are neither LDPE nor PCL thermal properties. These results indicate that the LDPE and PCL have physically interacted. Based on DSC analysis, it is known that there has been a decrease in the thermal properties of LDPE after mixing with PCL, which produces a polyblend. Previous studies have also stated that the addition of PCL to polymeric materials will reduce the thermal properties of the resulting polyblends.²¹

Scanning Electron Microscopy (SEM) Analysis

The SEM test was conducted to determine the morphological differences between pure LDPE and the LDPE/PCL polyblend. The results of the SEM photo analysis are shown in Fig.-5 below.

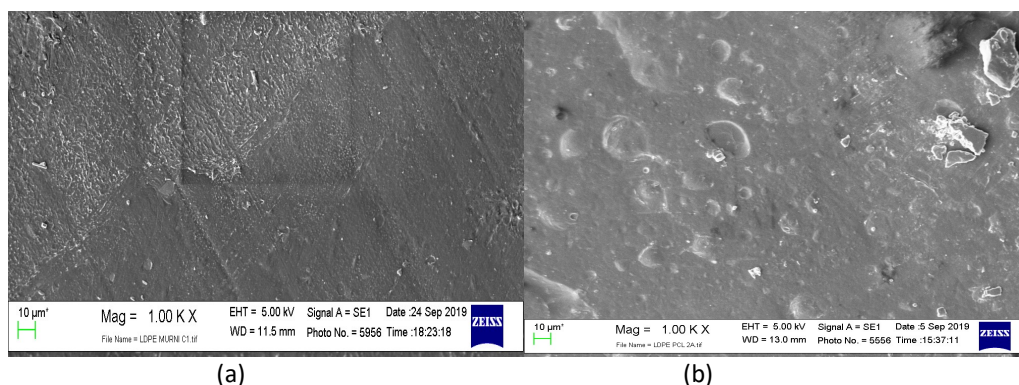


Fig.-5: SEM Analysis Results of Plastic Specimens, (a) Pure LDPE; and (b) LDPE/PCL Polyblend

Figure-5(a) presents a pure LDPE specimen. The results of the analysis showed that the surface still tends to be smooth and there are no lumps. This is because PCL has not been added to the LDPE matrix.²⁷ Next, in Fig.-5(b), an LDPE/PCL polyblend is presented. The results of the analysis showed the presence of a rough surface and the presence of lumps. This is because the PCL mixture has filled the voids on the LDPE surface. In addition, the spread of PCL on LDPE also seems to have been evenly distributed and homogeneous.⁸ In addition, there has been a physical interaction between LDPE and PCL

Biodegradation Test on Waste Soil

The rate of degradation of polyblends on used soil was measured by observing changes in the weight of the specimens for 60 days, the results of which are presented in Fig.-6.

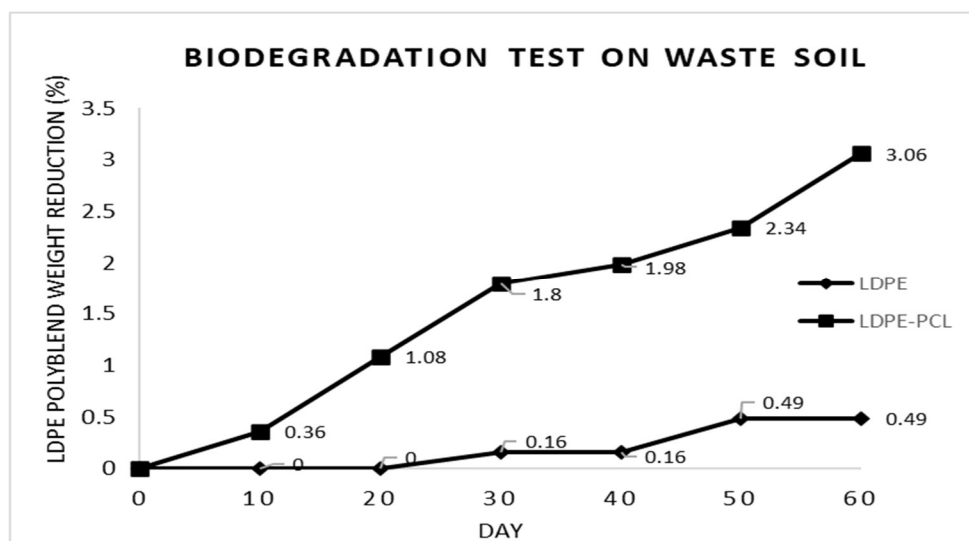


Fig.-6: Data on Changes in Specimen Weight during Burial in Soil

Based on the data in Fig.-6, LDPE/PCL polyblend specimens degrade faster than pure LDPE specimens. The difference in the rate of degradation between LDPE/PCL polyblend and pure LDPE was not very significant. On day 60, the LDPE/PCL plastic specimen had a degradation rate of 3.06%. Whereas, pure LDPE plastic specimens had a degradation rate of only 0.49%. On the other hand, the high degree of polyblend crystallinity is one of the causes of the low degradation rate of LDPE/PCL polyblends. The higher the degree of crystallinity of a material, the higher the tensile strength of the material increases. This is also related to the stronger interaction between LDPE and PCL. Consequently, it is difficult to interfere with the interactions that occur between LDPE and PCL. The environmental conditions of the polyblend planting sites are also a factor causing the low rate of degradation. If the planting of polyblend is done directly in the open, the possibility of the polyblend being degraded is greater. Abiotic factors such as rain, sunlight, dew, and humidity can affect the rate of degradation. Whereas, biotic factors such as microorganisms that

continue to change and even increase can also affect the rate of polyblend degradation. Some bacteria that can degrade LDPE/PCL polyblend plastic film are *Staphylococcus sp.*, *Pseudomonas sp.*, *Streptomyces sp.*, *Bacillus sp.*,²⁸ *Clostridium botulinum*, and *Clostridium acetobutylicum*.² While the fungal species that can degrade LDPE/PCL polyblends are *Aspergillus*, *Fusarium*, *Penicillium*, and *Parangyodontium*.²⁹

CONCLUSION

The mixing of LDPE with PCL obtained using a bis (dbzm)₂Zr catalyst has been successfully carried out using the reflux technique. The most compatible polyblend mixture was obtained at a ratio of 10/4 (w/w%) with a tensile strength value of 5.19 MPa and an elongation value of 25.18%. The resulting polyblend is semicrystalline and has lower thermal properties than pure LDPE. In this study, the LDPE/PCL polyblend has a single melting point which is neither the melting point of LDPE nor PCL. Next, SEM analysis also showed that the PCL mixture had filled the voids on the LDPE surface. These results indicate that LDPE and PCL have physically interacted and produced a polyblend. On the other hand, the resulting LDPE/PCL polyblend is more easily degraded than pure LDPE. The results of this biodegradation test show that the LDPE/PCL polyblend can be used as an environmentally friendly polymer and can minimize polymer waste in nature.

ACKNOWLEDGMENT

This research was funded by “Hibah PDUPT 2020” DRPM Kemenristek/BRIN RI (No.190/SP2H/AMD/LT/DRPM/2020). The authors would like to thank all the support that has been given.

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[RJC-6673/2021]