Innovation of Poly (Lactic Acid)/Carbon Black Composite as an Environment-Friendly Antistatic Packaging

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ABSTRACT

Antistatic packaging mainly protects an electronic device from damage caused by electronic discharge. However, antistatic packaging is typically made with a polymer which hard to decompose naturally. This property can badly affect our environments considering our daily activities produce a lot of plastic waste. Therefore, environmentally friendly antistatic packaging could potentially alleviate several plastic wastes generated. Antistatic packaging is made of conductive polymer composite (CPC) with poly(-lactic- acid)/PLA as its matrics have a biodegradable characteristic, biocompatibility, and resistance to thermal and chemical influence. And the use of Carbon Black as its filler can increase the electrical conductivity of CPC. Carbon black (CB) is synthesized by burning coconut shells and activating H_2SO_4. The synthesis of CPC samples was carried out by two methods; melt blending using a mini extruder and solvent blending using chloroform as a solvent. For solvent blending, a magnetic stirrer is used to homogenize the mixture running at 650 rpm and 60 °C. The filler composition was varied, namely 0, 0.5, 0.1, 1.5% by weight of PLA for melt blending and 0, 1.5% by weight of PLA for solvent blending. DSC tested the thermal properties of the sample. It was found that the melting temperature of the samples was not much different from that of pure PLA with a difference of 0.4-2.2°C. From the FTIR test, it is known that the solvent has been completely removed from the sample, and the conductivity test shows an increase in conductivity along with the addition of filler from $9{,}505x10^{-12}$ S/cm to $5{,}752x10^{-7}$ S/cm and $9{,}872x10^{-12}$ S/cm to $1{,}034x10^{-6}$ S/cm for melt and solvent method.

1. Introduction

Conductive materials demand for electronic devices such as sensors, touch screens, light-emitting diode, electromagnetic interference (EMI) shielding, antistatic packaging, and super-capacity are increasing along with the rapid development of technology. As known, electronic devices are very sensitive and easily damaged by electronic discharge. One of the protections is the use of antistatic packaging for the shipping process. Unfortunately, the common antistatic packaging also contributed to environmental problems and required special treatment because it couldn't decompose naturally. Based on World Bank data, Indonesia produced around 66-67 million tons of waste in 2019, of which around 15% is plastic waste [1].

Indonesia also annually produces 15.5 billion of coconut, which is equivalent to 3.02 million tons of copra, 3.75 million tons of water, 0.75 million tons of shell charcoal, 1.8 million tons of coir fiber, and 3.3 million tons of coir dust [2]. The coconut fruit processing industry is generally still focused on processing fruit flesh as the main product, while industries that process fruit by-products such as;

water, coir, and coconut shells are still traditional and on a small scale, even though they have a large potential for the availability of raw materials for other derivative industries.

One of the efforts to reduce the impact of conventional plastic waste is the use of biodegradable polymers. Poly(lactic acid)/PLA is a promising alternative to replace conventional polymers because it has relatively the same mechanical properties, especially in packaging applications. The excellent properties of poly(lactic acid) include biodegradability, biocompatibility, and resistance to thermal and chemical influences. The degradability of PLA can be modified by changing its microstructure [3] or mixing it with other polymers, additives, plasticizers, and some other inorganic fillers [4]. PLA is an insulator so filler is needed to increase its conductivity for application on antistatic packaging.

Carbon Black (CB) is a filler that is often used to increase the electrical conductivity of plastics in use as packaging for electronic devices. The packaging prevents the discharge of static electricity so that the electrical components inside do not experience dielectric disturbances or short circuits [5, 6]. Leng et al. reported that CB can be distributed homogeneously in the polymer matrix and has proven to increase in electrical conductivity of polymer [7]. CB can be produced through the shell carbonization process, followed by the activation stage using H_3PO_4 solution, and reduced in size as needed [8].

The distribution of the filler into the polymer matrix results in a new material known as CPC due to the higher electrical conductivity of the neat polymer. CPC with a certain electrical conductivity range can be used as antistatic packaging [9]. Considering the excellent properties of poly(lactic acid)/PLA, the development of CPC using PLA as a matrix is interesting to investigate. In this study, CB as a filler is made by carrying out a series of processes on coconut shells. There are two mixing methods of PLA/CB used in this study, namely, melt blending and solvent blending. Finally, the obtained CPCs were subjected to several tests, including structural characterization, thermal and electrical conductivity tests.

2. Research Methodology

2.1. Materials and Tools

Poly(lactic acid) was purchased from Shenzhen Cadit Plastic Material Co., Ltd., with a commercial named CADIT KD-195. This PLA, in granular form, has a glass transition temperature (Tg) at 60-62 ^oC. the obtained CB from the treatment of coconut shells was used as the filler. Chloroform as the solvent and Sulfuric acid were supplied by Anhui Fulltime and Sigma-Aldrich. All materials in this study were used without purification.

Composites were prepared via melt blending in a mini single screw extruder at 180 ^oC (Wellzoom type B). While the preparation via solvent blending, this process was carried out at room temperature with chloroform as the solvent.

2.2. Research Flow Diagram

2.2.1 Carbon Black Production from Coconut Shells

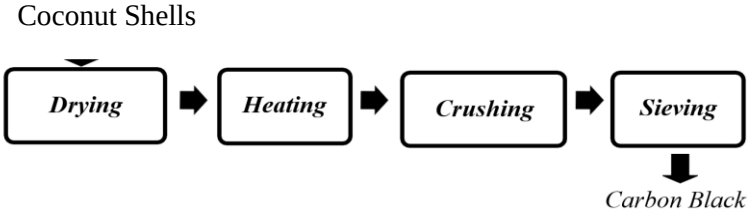


Fig. 1. Carbon Black Production from Coconut Shells

2.2.2 Melt Blending Method

Fig. 2. Synthetic Scheme of Conductive Polymer Composite via Melt Blending Method

2.2.3 Solvent Blending Method

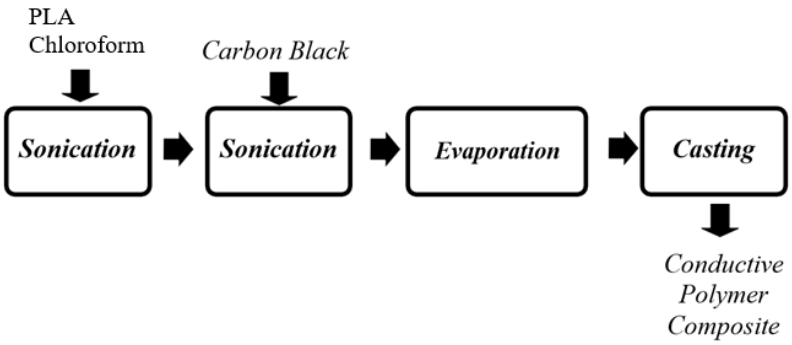


Fig. 3. Synthetic Scheme of Conductive Polymer Composite via Solvent Blending Method

2.3. Research Steps

The research steps are as follows:

2.3.1 Carbon Black Production from Coconut Shells

Coconut shells are converted into charcoal powder via the combustion method. Six kilograms of coconut shells are dried in the sun for 1 day. Furthermore, the roasting process is carried out at a temperature of 348 °C until the coconut shell does not produce smoke. Pounding and sieving were carried out to obtain CB powder with a size of about 200 mesh. Furthermore, the activation process is carried out by adding H_2SO_4 and drying using an oven.

2.3.2 Melt Blending Method

PLA and carbon black were put into the extruder simultaneously at 180 °C and 200 rpm. The composition of CB was varied 0, 0.05, 0.1 and 0.15 wt% (see Table 1). A fiber-shaped composite with a diameter of 3 mm will be produced in this mini single screw extruder. Finally, the CPCs are cut into pieces with a length of 4 cm before characterizing their properties.

2.3.3 Solvent Blending Method

In the solvent blending method, 10 grams of pol (lactic acid) is mixed with 175 mL of chloroform (solvent) in an Erlenmeyer and heated on a heat magnetic strirrer at 60°C and 250 rpm for 4 hours. Carbon black was added with variations of 0 and 1.5 wt% and stirred again for 1 hour (see Table 1). The stirring solution was left in the fume hood for a while to evaporate the chloroform until it became a more viscous solution. The viscous solution was then poured into glass molds with a thickness of 2 mm and left in a fume hood for 1 day. The dried CPC sheets were then cut into pieces with a size of 2x2 cm.

Table 1. List of the samples prepared for this study

Sample	Process	Condition	Composition, %wt	
			Poly(lactic acid)	***Carbon Black***
MPLA0	Melt Blending	180 ºC	100	0
MPLA05	Melt Blending	180 ºC	99.5	0.5
MPLA10	Melt Blending	180 ºC	99	1
MPLA15	Melt Blending	180 ºC	98.5	1.5
SPLA0	Solvent Blending	60 ºC	100	0
SPLA15	Solvent Blending	60 ºC	98.5	98.5

2.3.4 Sample Characterization

The characterization of samples was carried out to determine the molecular structure, thermal property, and electrical conductivity. The functional groups of CPC were identified by the Fourier-Transform Infrared Spectrometer (FTIR), and the Shimadzu IR Spirit. Differential Scanning Calorimetry (DSC), Shimadzu DSC60 was used to analyze the thermal properties and crystallinity of CPC. The DSC test was operated by a heating rate of 10 ºC/min in a temperature

range of 30-300 ºC. The electrical conductivity was determined by Keithley 2602A SYSTEM SourceMeter in a voltage range of 0-1 V.

3. Results and Discussion

3.1. Carbon Black (CB)

Carbon Black synthesis is carried out by roasting coconut shells. The obtained charcoal is reduced in size to about 200 mesh before activation The activation process is carried out by soaking the CB powder in a sulfuric acid solution. The carbon black is then dried and ready to be used as a filler in composites (Fig. 4).

Fig. 4. Synthesized Carbon Black

3.2. Conductive Polymer Composite via Melt Blending

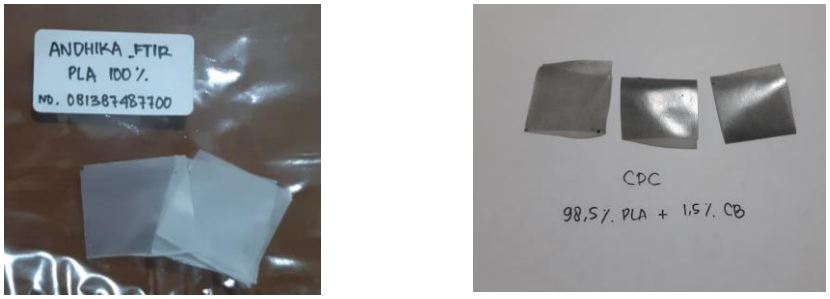
Synthesis of Conductive Polymer Composite (CPC) was carried out via melt blending method using a mini single screw extruder. The composition of carbon black (CB) was varied 0, 0.5, 1 and 1.5 wt% (see Fig.5). Visually, increasing the carbon black ratio makes the CPC color darker.

(a) (b) (c) (d)

Fig. 5. Samples Prepared via Melt Blending with various CB compositions; (a) MPLA0 (b) MPLA05 (c) MPLA10 (d) MPLA15

3.3. Conductive Polymer Composite via Solvent Blending

CPC synthesis through solvent blending was carried out with chloroform as solvent The composition of carbon black (CB) varied 0 and 1.5% for this method. After the CB was added to the PLA solution, the mixture was left in the fume hood for a moment until a viscous solution was obtained. The mixture was then poured into a glass mold The chloroform was allowed to evaporate in the open air (placed in a fume hood) for 24 hours and left on the CPC sheets (Fig.6).



(a) (b)

Fig. 6. Samples Prepared via Solvent Blending with Various CB compositions: (a) SPLA0 (b) SPLA15

3.4. Fourier-Transform Infrared Spectrometer (FTIR) Test

The FTIR test was carried out to determine the functional groups of the CPC samples. In Fig.7 it can be seen that each sample shows the same pattern and there is no significant difference between pure PLA and CPC samples. This shows that the melting and mixing process of CB in the extruder tends not to change the polymer structure.

In the solvent blending method, the chloroform content was removed by drying open air in a fume hood for 24 hours. The results of the functional group test showed that there was no functional group indicating the presence of chloroform. FTIR spectra for samples using the solvent blending method (Fig. 8.) show no difference between pure PLA and CPC samples. This indicates the chloroform has evaporated completely and does not damage the structure of the PLA.

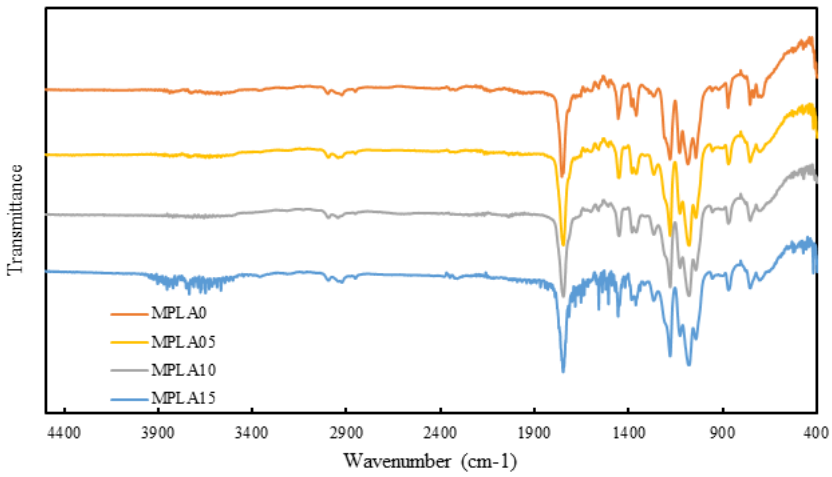


Fig. 7. ATR-FTIR of Samples Prepared via Melt Blending

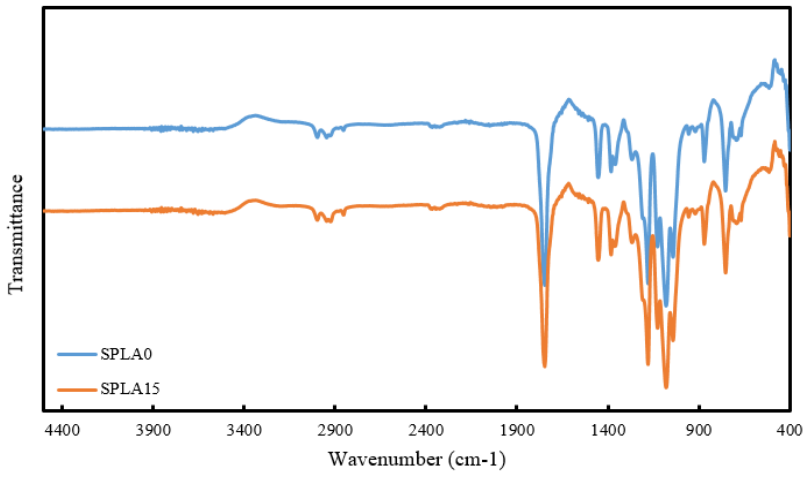


Fig. 8. ATR-FTIR of SamplesPrepared via Solvent Blending

3.5. Thermal Test

Melting temperature (Tm) can be defined as the peak temperature on the DSC thermogram. Table 1. shows that the melting temperature of CPC tends to increase slowly with increasing CB filler content, except for the MPLA15. Melting temperature can be affected by intermolecular forces, chain flexibility and crystallinity [10]. The low T_m in the MPLA15 sample is probably due to the addition of 1.5wt% CB is too much and it causes reduces intermolecular forces and chain flexibility, although crystallinity increases.

Table 2. Thermal Data of Samples Determined from Differential Scanning Calorimetry (DSC)

Sampel	Tg, ˚C	Tm, ˚C	Entalpi, J/g	Xc, %
MPLA0	NA	171.56	-40.69	43,426
MPLA05	NA	171.93	-40.64	43,590
MPLA10	NA	172.04	-40.05	43,175
MPLA15	NA	169.39	-40.66	44,055
SPLA0	60,64	173.91	-38.79	15,816
SPLA15	59,20	174.64	-39.37	17,585

The glass transition temperature (Tg) did not appear in the samples prepared using melt blending, It may due to degradation or chain breaking in poly(lactic acid). It can be seen in Table 1 that there is no significant difference in Tg and Tm between samples with filler and neat PLA, which indicates that the presence of filler does not significantly affect the thermal properties of the addition of filler in the range of 0-1.5%.

The addition of filler to poly-(lactic acid) only caused a difference in enthalpy of fusion with pure PLA between 0.03-0.64 J/g. The enthalpy of melting is the value obtained from the area at the peak of the melting point graph. This enthalpy value can be used to calculate the crystallinity of the obtained CPC samples. The degree of crystallization (Xc) of the samples could be acquired with the following equation,

$$Xc = \frac{\Delta H_m - \Delta H_{cc}}{x \,.\, \Delta H^{\circ}_m} \,.\, 100\% \qquad [11]$$

which ΔH_m and ΔH_{cc} are the enthalpy of fusion and enthalpy of cold crystallization, respectively, x is the fraction of PLA in the CPC and H˚m of PLA is 93.7 J/g. The degree of crystallinity tends to increase with the increase in the amount of filler in the CPC. This means that CB filler can be a nucleating agent and accelerate crystallization.

Conductivity Test

Electrical conductivity measurement, as presented in Figure 9, shows that the samples prepared via solvent blending had a higher conductivity than that of sample prepared via melt blending. It can be seen at the same composition of CB. SPLA15 has electrical conductivity about 1.034×10^{-6} S/cm, while MPLA has a lower value of about 5.752×10^{-7} S/cm.

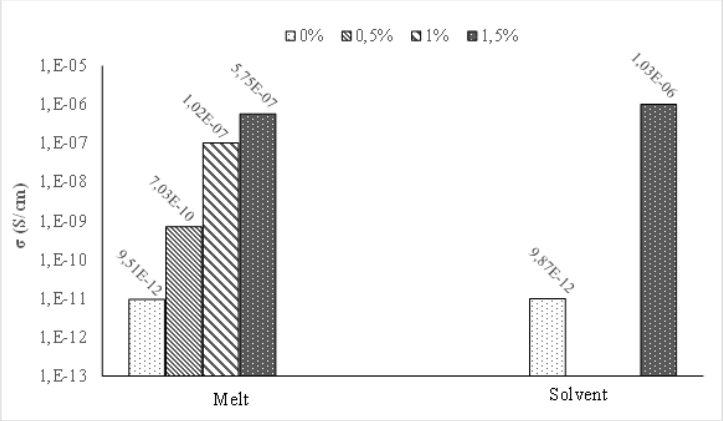


Fig. 9. Electrical Conductivity Measurement Result of Samples

According to Braga [12] and de Souva Vieira [13], materials with conductivity between 10^{-11} to 10^{-6} S/cm can dissipate static electricity slowly, so they can be applied as antistatic packaging. From the samples tested, CPC with various filler levels showed resistivity values that met the requirements for use as antistatic packaging.

4. Conclusion

The results of the FTIR test showed that there was no significant change in the functional groups between CPC and neat PLA, so the properties of PLA do not change significantly. In addition, the thermal analysis showed that the CB as filler may act as a nucleating agent. Based on the measured electrical conductivity, CPC made by adding CB to PLA has the potential to be used as environmentally friendly antistatic packaging.

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