Formulation of mono-diacylglycerol from palm fatty acid distillate and glycerol as antistatic agents on plastics

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Abstract. Palm Fatty Acid Distillate (PFAD) can be increased its added value by converted to mono-diacylglycerol (MDAG). MDAG has free hydroxyl groups which make it possible as antistatic agent in plastics. Antistatic is main additive in plastic products, which can reduce the tendency of static electricity. This study aims to obtained the best formulation of MDAG as an antistatic agent in plastics. The methods of this study included formulation of MDAG in plastic polymer, injection molding process and measurement of surface resistivity. The formulation of MDAG in plastic polymers (PP, HDPE, LDPE) have been done in three steps. First, commercial antistatic and MDAG (3.80% FFA content) was added to polymers for injection molding process. There were no antistatic properties detected of MDAG plastic plates. Meanwhile the commercial antistatic shows there were antistatic properties on its plates. The second formulation was using MDAG with better characteristics which has no FFA content. Both MDAG and commercial antistatic showed antistatic properties on PP plates with similar surface resistivity, which was 10^12 Ω/sq. Third formulation was using the same MDAG in PP and HDPE polymer and its surface resistivity was observed for several days. Both MDAG and commercial antistatic showed antistatic properties on each plate, with the range of surface resistivity at 10^11-10^12 Ω/sq. There were significant differences of antistatic activities in PP and HDPE plates, where antistatic properties in PP plates was immediately detected dan faster than HDPE plates. It can be caused by the difference between PP and HDPE density that influence the migration rate of antistatic agent to the surface. In this third stage, it was also created the MDAG masterbatch by mixing MDAG and LDPE polymer, which showed antistatic properties on HDPE plates after several days, with the range of surface resistivity at 10^12 Ω/sq. The measurement of surface resistivity on each plastic plates showed that MDAG has antistatic properties, as well as commercial product.

Keywords: mono-diacylglycerol, antistatic, plastic, biocomposite

1. Introduction

Indonesia is one of the largest CPO (crude palm oil) producer in the world with total production in 2017 is 35 million tons [1]. The by-product of the CPO refining process is palm fatty acid distillate (PFAD). The high production of PFAD makes PFAD as an attractive commodity to be increased its added value by making it to mono-diacylglycerol (MDAG). MDAG is an ester from glycerol with free fatty acid which have unreacted/free hydroxyl groups. MDAG is combination of monoglycerides compound (MAG), which has one acyl chain and diglyceride (DAG), which has two fatty acyl chains.
[2]. Monoacylglycerol has two free hydroxyl groups, while diacylglycerol has one free hydroxyl group. This free hydroxyl group makes MDAG as a non-ionic surfactant which is biodegradable, biocompatible and non-irritant, which is commonly used in the food, cosmetics and pharmaceutical industries. In addition, this free hydroxyl groups makes MDAG possible as an antistatic agent, both in bio-composite material and in plastics.  

To form plastic characteristics as needed, additive such as plasticizers, stabilizers, antistatic, lubricants, dyes, fillers and fire retardants are added to the plastic polymer [3]. Plastic production cannot be separated from the needs of antistatic agents, especially for plastics sheet and electronic equipment. Antistatic agent is one of the most important additives in plastic products which is needed to replace the static electricity between two different materials, or plastic surfaces. Static electricity is formed by excess electrons on the surface. This imbalance can be created by the friction of two materials or through the induction process with ionized air [4]. MDAG has free hydroxyl groups which has hydrophilic properties which makes the thin layer on the surface and reduce the surface conductivity thereby avoid the accumulation of static electricity on the surface.

One of antistatic products that is widely used commercially is GMS (glycerol mono-stearate). GMS also has free hydroxyl groups as antistatic agents like MDAG. The need for GMS is quite large, but so far, there is no GMS from local products that can compete, even though the raw material for making this emulsifier are available in large quantities in the country. One of the reasons is the price that is not competitive compared to import products, due to high processing costs and enzyme catalysts.

MDAG in this study was synthesized using glycerol and PFAD through esterification process using acid catalysts that relatively easy to find at commercial market with affordable prices. Therefore, this study aims to looking for the best formulation of MDAG as an antistatic agent in plastics.

2. Materials and Methods

2.1. Materials

The materials used in the study were MDAG, commercial MDAG namely Dimodan HR, Dimodan HPM and GMS40, polypropylene (PP-AY564), high density polyethylene (HDPE-5218), low density polyethylene (LDPE), plastic injection molding machine and Work Surface Tester ST-4 (Simco, Japan).  

2.2. Methods

The methods used include the formulation of MDAG in plastics polymer, the injection moulding process and the measurement of surface resistivity.

2.2.1. Formulation of MDAG in plastics polymer

The MDAG concentration in plastic polymer was determined. MDAG and polymer weighed, mixed in plastic bags and shaken until homogenous.

2.2.2. Injection Moulding Process

Injection moulding process using the plastic injection moulding machine at PT DIC Astra Chemicals. The antistatic sample (MDAG and commercial antistatic) was mixed with the plastics polymer and then poured through inlet of injection moulding machine. The mixed polymer will be injected at 235 °C and moulded into square plastic plates (± 10 x 5 cm).

2.2.3. Measurement of Surface Resistivity of Each Plate

The plastic plates from injection moulding process was left for a moment until the temperature decrease (room temperature, ± 25 °C). Each plate was measured its surface resistivity using Work Surface Tester ST-4 (Simco, Japan). The surface resistivity number that showed by the instrument was expressed in Ohm/square (Ω/sq).
3. Results and Discussion

3.1. First Formulation of Antistatic in Plastic Polymer

The first formulation of antistatic in plastic polymer was used three antistatics, which is Dimodan HR, Dimodan HPM and MDAG. Dimodan HR and Dimodan HPM is one of commercial MDAG. Dimodan HR is from hydrogenated rapeseed oil that has 96% monoglycerides as its main component. Meanwhile, Dimodan HPM is from hydrogenated palm-based oil that has 97% monoglycerides. The plastic polymer used are PP and HDPE. The addition of antistatic agent usually at the range of 0.1-1.0% [5]. On this formulation, the addition of antistatic was 1% (w/w) of the plastics polymer. So, there are eight plastics samples namely PP (without addition of antistatic), PP + Dimodan HR, PP + Dimodan HPM and PP + MDAG. there are HDPE (without addition of antistatic), HDPE + Dimodan HR, HDPE + Dimodan HPM and HDPE + MDAG. The visual appearance of those plastic plates can be seen in Figure 1 and Figure 2. The injection of 300 g polymer usually formed 5-7 square plates with the size of ± 10 x 5 cm. While the surface resistivity of each plate can be seen in Table 1 and Table 2.

![Figure 1. The visual display of first formulation-PP plates (from left to right): PP without antistatic, PP + Dimodan HR, PP + Dimodan HPM and PP + MDAG](image1)

![Figure 2. The visual display of first formulation-HDPE plates (from left to right): HDPE without antistatic, HDPE + Dimodan HR, HDPE + Dimodan HPM and HDPE + MDAG](image2)
The visual appearance of PP plates shows that PP with the addition of MDAG has yellowish color than PP without additive (as a control) and PP with the addition of commercial antistatic (Dimodan HR and Dimodan HPM), so do HDPE plates. This is caused by the yellowish color of MDAG, which comes from purification process that has not been optimal and bring the PFAD natural color. The yellowish color of MDAG can be eliminated by optimizing the purification process before formulation with plastic polymer. Meanwhile, there is no significant differences of the plates texture from the control (plastic polymer without additive) than plates with the addition of Dimodan HR, Dimodan HPM and MDAG.

MDAG as antistatic agent will diffuse to the surface and attract the water molecule on the surface. Free hydroxyl groups in MDAG which is hydrophilic will cause the formation of thin layer of water on the surface, which will reduce the surface resistivity and prevent the accumulation of static electricity. Antistatic agent reduced the surface resistivity on range 10^{10} until 10^{13} Ω/sq [6][7]. So, the antistatic properties in each plate can be observed by measure the surface resistivity of the plate.

The surface resistivity was varied for each sample. The measurement of PP plates in Table 1 showed that PP with the addition of Dimodan HR and Dimodan HPM have the same surface resistivity, which was on the range of 10^{11} Ω/sq. Meanwhile, PP without additive and with the addition of MDAG have the same surface resistivity of 10^{13} Ω/sq. These results show that PP without additive has the accurate number as the surface resistivity of pure plastic polymer, which is 10^{13} Ω/sq [9]. Then, there is antistatic properties on the plates of PP + Dimodan HR and PP + Dimodan HPM. Meanwhile, the addition of MDAG does not give antistatic properties to PP plates. This can be caused by several things, such as free fatty acid content in MDAG still high. The low hydroxyl number also affect the absence of antistatic properties on plastics. The hydroxyl number shows amount of free hydroxyl groups in a surfactant [8]. The higher hydroxyl number means the better antistatic characteristic of MDAG.

Meanwhile, the measurement of HDPE plates in Table 2 show almost similar results. HDPE plates without antistatic and with the addition of MDAG does not have antistatic properties. And HDPE plates with the addition of commercial MDAG has antistatic properties. But in some plates of HDPE + Dimodan HPM, the antistatic properties were not detected. This can be caused by the difference of migration rate of PP and HDPE. The migration rate of antistatic to the surfaces is influenced by the density and crystallinity of polymer [9]. The higher density of HDPE than PP makes the migration is slowly on HDPE surfaces, the formation of antistatic layer on the surface will also slowly and the decrease of surface resistivity will spend longer time than on PP. The improvement of

| Table 1. Surface resistivity of PP plates (first formulation) |
|---------------------------------------------------------------|
| Formulation             | Surface Resistivity (Ω/sq) |
|-------------------------|-----------------------------|
| PP                      | 2.5–3.2 x 10^{13}           |
| PP + Dimodan HR         | 2.5 x 10^{10}–2.0 x 10^{11} |
| PP + Dimodan HPM        | 1.0 x 10^{10}–1.0 x 10^{11} |
| PP + MDAG research      | 1.6–3.2 x 10^{13}           |

| Table 2. Surface resistivity of HDPE plates (first formulation) |
|---------------------------------------------------------------|
| Formulation             | Surface Resistivity (Ω/sq) |
|-------------------------|-----------------------------|
| HDPE                    | 3.2 x 10^{13}               |
| HDPE + Dimodan HR       | 1.3 x 10^{10}–4.0 x 10^{12} |
| HDPE + Dimodan HPM      | 2.5 x 10^{12}–3.2 x 10^{13} |
| HDPE + MDAG research    | 1.6–3.2 x 10^{13}           |
The synthesis and purification process of MDAG was done to obtain MDAG with better characteristics, then it is used in second formulation on plastic polymer.

3.2. Second Formulation of Antistatic in Plastic Polymer

On the second formulation, MDAG was obtained from the improved synthesis and purification process. This MDAG has low free fatty acid content (0.51%), high hydroxyl number (349.33 mg KOH/g) and high purity (93.29 % monoglycerides). The commercial antistatic which is used are GMS40 and Dimodan HPM. Meanwhile, the plastics polymer which used is PP. On this formulation, the addition of antistatic was 0.1% of plastics polymer. So, there are PP + GMS40, PP + Dimodan HPM, PP + MDAG (I) and (II).

The visual appearance of the plastic plates can be seen in Figure 3. They are all same in bright white color. The improvement of synthesis and purification process of MDAG produced MDAG with better characteristics. The brighter color and dry texture of MDAG, make it looks similar with the commercial product, so that those plates has similar visual characteristics. The surface resistivity of each plate can be seen in Table 3. The surface resistivity number was $10^{12} \Omega$/sq which showed that both MDAG and commercial antistatics has antistatic properties in PP plates.

![Figure 3. The visual appearance of second formulation-PP plates (PP + GMS40, PP + Dimodan HPM, PP + MDAG)](image)

| Formulation                  | Surface Resistivity (\(\Omega/sq\)) |
|------------------------------|------------------------------------|
| PP + GMS 40                  | $1\text{--}1.3 \times 10^{12}$     |
| PP + Dimodan HPM             | $1\text{--}2 \times 10^{12}$       |
| PP + MDAG-research (I)       | $1\text{--}2.5 \times 10^{12}$     |
| PP + MDAG-research (II)      | $1\text{--}3.2 \times 10^{12}$     |

3.3. Third Formulation of Antistatic in Plastic Polymer

On this formulation, the antistatic properties on each plate was observed for several days. The antistatic agent used included GMS40 and MDAG. Meanwhile, the plastics polymer which used are PP, HDPE and LDPE (for masterbatch production only). The addition of antistatic was 0.1% of PP and 0.3% of HDPE polymer. So, there are PP + GMS40, PP + MDAG (I) and (II), HDPE + GMS40, HDPE + MDAG (I) and (II).
The surface resistivity of each plate was displayed in figure 4 and figure 5. The surface resistivity of PP plates was observed until 25th day, meanwhile HDPE plates until 13th day. The antistatic migration of each plate was fluctuating. However, the differences of antistatic activities on PP and HDPE surface plates was significant. On the PP plates, antistatic properties detected on the first day after plate was moulded. Meanwhile, on some HDPE plates, antistatic properties detected on the fourth and fifth day. This showed the differences of migration rate of antistatic in each polymer. The migration rate is influenced by the density of polymer. PP-AY564 which is used in this study has the density of 0.90 g/cm³ (The Poliolrfyn Company, SG) and HDPE-5218 has the density of 0.952 g/cm³ (Rigidex, EU). This difference caused antistatic on PP migrates faster than HDPE polymer. Therefore, the detection of antistatic properties on PP plates was faster than on HDPE plates.

![Figure 4](image_url)

**Figure 4.** The antistatic activities on PP plates: (a) PP + GMS40, (b) PP + MDAG (I) and (c) PP + MDAG (II).
On this study, masterbatch of MDAG also created using masterbatch maker machine and pelletizer in PT DIC Astra Chemicals. Masterbatch was created by mixing MDAG and LDPE polymer, and then pour into inlet of masterbatch machine. Masterbatch machine consist of top feeder as charging material and single screw. On this study, LDPE polymer was chosen because it has a lowest density between PP and HDPE, in order to masterbatch can be mixed later with other polymers when injected into injection moulding. Masterbatch addition in plastics polymer usually around 5–25%. The MDAG on this study was added by 5% of LDPE polymer. The LDPE + 5% MDAG masterbatch resulting wet pellets. This can be caused by antistatic properties that bind the H₂O molecules when the masterbatch was passed on water at cooling down stage before forwarded into pelletizer.

The antistatic agents have a hydrophobic and a hydrophilic part. One part is compatibles with plastic polymer. The other part extends to the surface of the plastic and has bonding groups with water molecules, makes a molecular layer and decrease electrical resistance on the surface [10].

Therefore, the masterbatch pellet have to dried before put into injection moulding machine. The masterbatch pellet was dried at 85 °C for 1 hour, then it was mixed with HDPE using 5 % formulation and being injected to form 6 plates with different antistatic activities. The antistatic activities of this plate can be seen in figure 6. Antistatic properties of each plate from HDPE + masterbatch was detected on the third and fourth day after plates are moulded, with surface resistivity of 10^{12} Ω/sq.
4. Conclusions
The MDAG obtained from the improved synthesis and purification process have the same surface resistivity with commercial antistatic, which was $10^{12}$ $\Omega$/sq. The results of surface resistivity measurement on PP and HDPE plates, which added with MDAG and commercial antistatic showed antistatic properties in each plate with surface resistivity of $10^{11}$-$10^{12}$ $\Omega$/sq. There were significant differences of antistatic activities in PP and HDPE plates based on the differences on polymer density that influence the migration rate of antistatic agent to the plastic surface. The MDAG masterbatch (MDAG+LDPE) resulting wet pellet, due to the antistatic that bind water so it needs to be dried before being injected with HDPE, PP or others polymer. However, the antistatic properties of MDAG masterbatch in HDPE plates were detected on third day and fourth day, with surface resistivity of $10^{12}$ $\Omega$/sq. The measurement of surface resistivity on each plastic plates showed that MDAG has antistatic properties, as well as commercial antistatic.

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