Tensile properties of PolyLactic Acid Composite Foamed via Supercritical Carbon Dioxide

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Abstract. Tensile properties of foamed PolyLactic Acid (PLA) composite were studied. In this work, PLA were incorporate with Durian Skin Fibre (DSF) and Cinnamon Essential Oil (CEO) to form PLA bio composite and further treat via supercritical carbon dioxide (SCCO2) to form foamed PLA bio composite. The tensile strength value of foamed PLA bio composite slightly drops from foamed PLA. As for stress strain graph, the percentage of strain for foamed PLA and PLA bio composite did not distinct much. Through SEM, the foamed PLA bio composite showing that it did not fully foamed after treated via SCCO2 which due to treatment period and the thickness of the thin films.

1. Introduction
The majority of foams manufactured in the industry use petroleum-based thermoplastic matrices as raw materials, however owing to the scarcity of fossil resources, as well as the growth of environmental issues and related social concerns, biopolymer (bio based/biodegradable/biocompatible polymers) are employed (Villamil Jiménez et al., 2020b). PolyLactic Acid is type of materials that owns environmental friendly prospect and had a high demand nowadays it is known for its biodegradability, sustainability and biocompatibility. The study on incorporation of PLA with natural fibre has been broaden worldwide, such as pineapple leaf, durian skin, coir, Empty fruit Bunch, Mango seed and many more (Biagiotti et al., 2004). The incorporation of natural fibre into polymer matrix was focused because of few advantages of natural fibre own such as low environmental impact, low cost and it can be fully utilized instead of becoming agricultural waste (Anuar et al., 2018).

Durian Skin Fiber (DSF) was acquire from durian fruit, the waste from it skin are about 60 – 70% (Manshor et al., 2012) making it has high potential in contributing as agricultural waste. DSF own structure and properties that are nearly identical to those of other natural fibres, and it is expected that DSF will be suitable for use as a filler in bio composite materials, leading to a wide range of applications (Mohd Nordin et al., 2021).

Supercritical Carbon dioxide (SCCO2) is a supercritical fluid which both pressure and temperature are above the critical value (Yang et al., 2017). Extensive work has been done to study SCCO2 as foaming agent for polymeric materials such as PolyLactic Acid (Villamil Jiménez et al., 2020a),
Polypropylene (Bao et al., 2016) and PMMA (Arab-Baraghi et al., 2014). SCCO2 known for its non-flammable, chemically inert, non-toxic and the residue also easy to manage. The properties of foamed polymer matrix can be tune by varying the pressure and temperature of SCCO2, which made this blowing method have huge advantages compared to other blowing method (Chauvet et al., 2017).

During SCCO2 process, polymer solubilized in carbon dioxide (CO\(_2\)) at working pressure and temperature, which plasticizes the polymer and lowers its apparent glass transition temperature or melting point to the processing temperature (Xu & Huang, 2014). Later, CO\(_2\) is released by depressurization where thermodynamic instability induces supersaturation of CO\(_2\) dissolved in the polymer matrix, resulting in cell nucleation. The cells continue to expand until the polymer crystalline (the transformation of a substance into a glass). This phenomenon that can be linked to coalescence, the merging of components to create one mass or whole.

In this work, focused will be given on PLA/DSF bio composite foamed via SCCO2. The tensile properties and morphology of the foamed bio composite are studied by varying the pressure of SCCO2, with constant loading number of DSF and with the addition of Cinnamon Essential Oil(CEO) acting as plasticizing agent for the composite (Mohd Nordin et al., 2021).

2. Materials and Methodology

The solution casting process will be used to create the PLA bio composite thin film. The PLA biopolymer resin, (grade 4043D) supplied by NatureWorks® and chloroform, from Labscan with grade of A&R ratio mixture must be 1:10 with 5% of DSF content. CEO were produced by Tanamera, Kuala Lumpur with 5% content. As for DSF, the wasted durian skin was gathered from a local market in Sungai Buloh. To get its fibre, durian skin was washed, chopped, crushed, ground, and sieved using a \(\leq 90\) \(\mu\)m sieve.

To mix the composite evenly, the mixture will be placed into chloroform, which will function as a reagent. The sample will be vigorously agitated with a magnetic stirrer on a hot plate until totally dissolved and casted into the mould in thin film form. The PLA and DSF5 bio composite film will undergo supercritical carbon dioxide (SCCO2) process at same temperature but different pressure in 2 hours. The variable parameter list is shown in table 1.

| Table 1. Variable Parameter |
|-----------------------------|
| Samples | Parameter | |
|       | Temperature | Pressure |
| PLA   | 60°C        | 150 bar  |
| DSF5  | 60°C        | 150 bar  |
| PLA   | 60°C        | 200 bar  |
| DSF5  | 60°C        | 200 bar  |

Universal Testing Machine (Shimadzu Autograph AGS-X series) will be used to perform tensile tests on the foamed PLA and PLA bio composite with 10 mm/min crosshead and sample size according to ASTM D882. Five samples were tested for each composition and average is taken as the final results.

Scanning electron microscope (SEM) (JEOL 5600) was used to observe the morphology of foamed PLA bio composite through fracture surfaces of the composites from tensile test, the fracture surfaces was mounted on aluminium stub and sputter coated with palladium (Pd) to avoid electrostatic charging during scanning.

3. Results and Discussions

3.1 Results

Figure 1 depicts the tensile strength of foamed PLA and PLA bio composite. Tensile strength for foamed PLA and PLA bio composite was found to be somewhat lower following the addition of 5% DSF and
Despite high DSF fibre content, the tensile strength value did not drop significantly as reported from previous study compared to untreated PLA bio composite. As mentioned by (Busu et al., 2015), tensile strength of PLA composites is expected to significantly dropped when high loading fibre were incorporated into PLA matrix. The idea of tensile strength that not significantly descent might due to SCCO2 treatment, this is because there are several paper have reported that SCCO2 contribute to plasticizing effect on polymer composite matrix (Zhao et al., 2013).

Due to this plasticizing effect, it also leads to less significant reduction on the stress-strain graph. Even though CEO has been incorporated into PLA bio composite for acting as plasticizing agent (Jamshidian et al., 2012), SCCO2 treatment also support this effect by chance. However, the stress-strain for both composite, DSF5 6.15 and DSF5 6.2 showing about the same value as shown in Figure 2.

Through SEM images in figure 3, the DSF presence can be noticed (in circles) well incorporated within the PLA matrix. Other than noticing the presence of DSF in the composite, DSF5 6.15 and DSF5 6.2 are noted has started to nucleating (refer to arrows) however, it not further up to foamed structure. This might due to short SCCO2 treatment period and the thickness of the film is too thin. Past study showing that the thickness of their composites are around 1.0 to 3.00mm. But in this study, the thickness of the films is around 0.35-0.45 mm. The SCCO2 gas particles passing through the polymer matrix in
high speed, making the polymer matrix unable to entrap SCCO2 particle to form foam structure (Chauvet et al., 2017).

4. Conclusions

Through this study, it can be concluding that SCCO2 did affecting the properties of foamed PLA bio composite. Both pressure did not show significant outcome, this is due to the thickness of PLA bio composite films that too thin compare to other study done for this SCCO2 samples. Foaming process starting to happening but due to the short saturation time and thin samples, the foaming process only happen up to nucleating and did not further up to foamed structure. Through this, few amendments such as thicker samples and longer saturation time need to be done so the PLA bio composite can further process to form foam structure.

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