

Study on the plasticiser type for biobased microcrystalline cellulose filled polylactic acid composite

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Abstract. The aim of this work was to study the effect of different type of plasticisers, i.e., polyethylene glycol (PEG) and coconut oil (CO), on the properties of microcrystalline cellulose (MCC) filled polylactic acid (PLA) composite. The sample compounding was carried out via melt blending method. The properties of the plasticised MCC filled PLA composites were characterized by tensile, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). It was found that CO showed a better plasticising effect, with improvement in elongation at break by 12% as compared to neat PLA and higher decomposition temperature at 302°C.

1. Introduction

Poly(lactic acid) (PLA) is a biobased polymer derived from a renewable resource and has widely used in many applications such as packaging, consumer items and medical implants [1]. PLA has many advantages such as low toxicity, high mechanical strength, biocompatibility and biodegradable. However, its main drawbacks are its brittleness and poor thermal stability [2]. Many methods have been investigated, such as adding a reinforcement agent or additives, irradiation using electron beam etc to enhance the performance of PLA [3-4].

Microcrystalline cellulose (MCC) is a biodegradable polymer derived from renewable origin such as wood and is often used as reinforcing agent in composites, particularly to improve the stiffness and thermal stability of the material [5-6]. However, previous work showed that the tensile strength and elongation at break decreased with the addition of MCC [6]. Thus, plasticiser is added into PLA composite in order to improve the flexibility and reduce the friction during processing. Apart from it, it helps to enhance its elongation at break [7].

In this study, two types of plasticiser were evaluated: polyethylene glycol (PEG) and coconut oil (CO) were added at the dose of 10 wt%, respectively into the biobased MCC filled PLA composites. The plasticiser was expected to provide plasticising effect via interaction with the polymer chains and enhance the ductility of the composite. Biobased content of the composite was determined via the ASTM D6866. It was reported that generally a minimum 25% biobased content must be fulfilled in order to certify as a biobased product [8].



2. Experimental

2.1. Materials

The PLA 3051D in pellet form was obtained from NatureWork LLC. PEG 400 (brand R&M) and MCC (brand Sigma Aldrich), CO (brand ChemSoln) were purchased from Synertec Enterprise Kuala Lumpur.

2.2. Sample preparation

The melt blending process was carried out by using an internal mixer (Haake PolyLab System) at 180°C and 50 rpm, with a retention time of 10 min. Prior to melt blending, PLA and MCC were dried in an oven maintained at 70°C for 24 hr to remove the moisture. The dosage of MCC and plasticiser (PEG or CO) were set at 10 wt% each and the composites were designated as PLA, PLA/MCC/PEG, PLA/MCC/CO as shown in table 1. Rectangular composite sheets (12 x 15 cm) with a thickness of 1 mm were produced by using compression molding. The compound was filled in a mold and being compressed by a hot press machine (model: Moore E53) at 185°C. The hot press operation steps included a pre-heating for 8 min, the compression process for 3 min at a pressure of 150 bar and cooling for 8 min. The sheets were cut into dumbbell shape (type IV) for the tensile test.

Table 1. Formulation for composite

Sample	PLA(wt%)	MCC(wt%)	PEG(wt%)	CO(wt%)
PLA	100	0	0	0
PLA/MCC/PEG	80	10	10	0
PLA/MCC/CO	80	10	0	10

2.3. Characterisation

2.3.1. Thermal gravimetric analysis (TGA). The thermal stability of the sample was studied by using the Perkin Elmer Pyris 1(USA). The sample, weighing between 6-8 mg, was heated from 30 to 600°C at a rate of 20°C/min, under nitrogen atmosphere. The onset decomposition temperature was recorded.

2.3.2. Scanning electron microscope (SEM). Field emission SEM (model FEI QUANTA 400 F FESEM) was used to observe the surface and fracture morphology of the specimens. Specimens were coated with a thin layer of gold to prevent electrical charging during the examination.

2.3.3. Biobased carbon content. The biobased carbon content of the sheet sample was determined according to ASTM D6866-16 Method B using the accelerator mass spectrometry method. The required solid sample size was approximately 1 g.

2.4. Polymer Testing

Tensile test. The tensile properties were determined with an Instron model 3366 tester according to ASTM D638 at a cross head speed of 5 mm/min. The average of 5 measurements for the tensile strength (TS), elongation at break (EB) and Young's modulus (YM) were collected.

2.4.1. The TS was calculated by using the force divided by the initial cross-sectional area as shown in Eq.1.

$$TS = \frac{\text{Force}}{\text{Area}} \quad (1)$$

2.4.2. The EB was calculated by dividing the extension at break point by the original length as shown in Eq.2

$$EB = \frac{\text{Extension}}{\text{Length}} \times 100\% \quad (2)$$

2.4.3. The YM was the ratio of stress and strain as shown in Eq.3

$$YM = \frac{\text{tensile stress}}{\text{tensile strain}} \quad (3)$$

3. Results and discussion

3.1. Tensile test

Table 2 shows the tensile properties of the tested specimens. The PLA/MCC/CO composite showed deterioration in TS and YM, but improvement in EB. This finding is in accordance with the result reported by Mohapatra et al. [9]. The addition of CO plasticiser reduced the intermolecular forces along the polymer chains, which led to reduction in TS and YM, and at the same time, increased the flexibility as reflected in higher EB. In this study, PEG did not show any improvement as a plasticiser. This could be attributed to the insufficient interaction between the PEG and the MCC filled PLA composite. The previous study by Taib et al [10] reported the presence of PEG might have disturbed the fiber-matrix interaction, which caused the unplasticised PLA/fiber composite exhibited better tensile properties than the plasticised composite. However, CO has shown its great potential in plasticising the MCC filled PLA composite, the EB improved by 12% as compared to neat PLA.

Table 2. Tensile properties

Sample	TS(MPa)	EB(%)	YM(MPa)
PLA	56.2±1.37	22.6±3.78	393±14.1
PLA/MCC/PEG	26.8±2.07	12.2±1.53	349±9.88
PLA/MCC/CO	22.2±0.47	25.4±5.34	346±5.12

3.2. TGA

The thermal degradation data are tabulated in table 3 and the TGA curves are shown in figure 1. The CO plasticised MCC filled PLA exhibited higher thermal stability than its counterpart, PEG. The thermal degradation for PLA/MCC/CO began at 302°C, it also showed improvement compared to neat PLA at 290°C. The improvement showed by CO could be attributed to its higher onset decomposition temperature, 257°C against the PEG at 150°C [11-12]. Lu et al reported high stability was found in virgin CO due to its high content of saturated fatty acids [13].

Table 3. Thermal properties

Sample	Onset decomposition temperature (°C)	Residual weight% at 600°C
PLA	290	0
PLA/MCC/PEG	280	8.59
PLA/MCC/CO	302	5.24

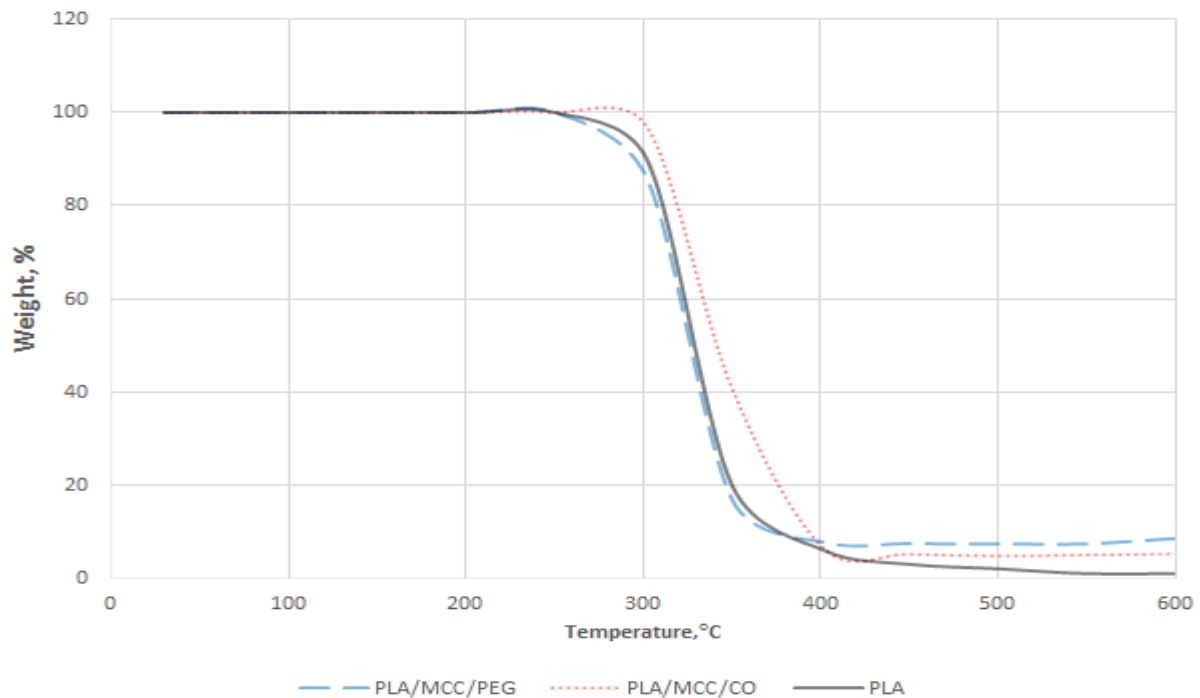
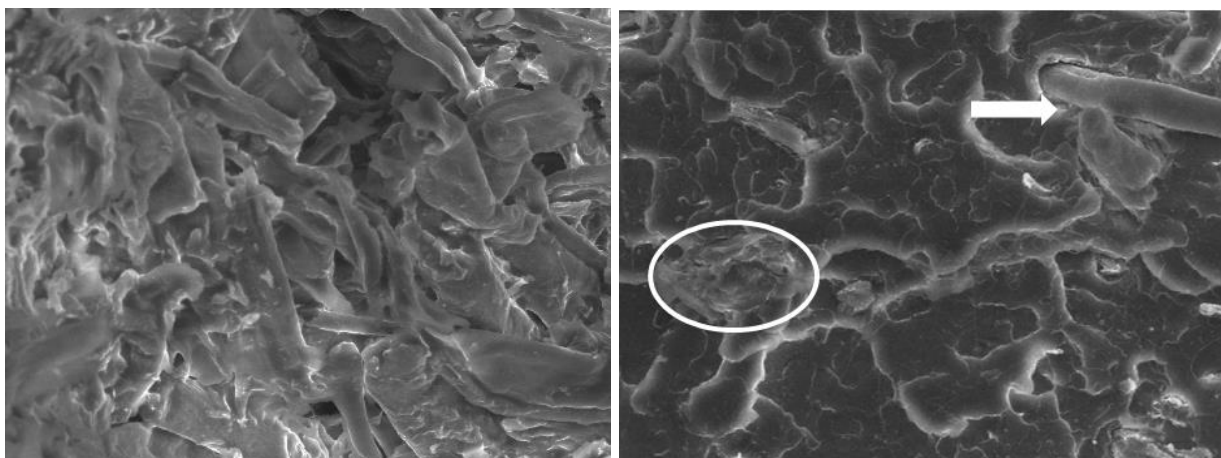


Figure 1. TGA curves

3.3. Morphology study

The SEM micrograph of the plasticised MCC filled PLA is showed in figure 2 (a) for CO and (b) PEG. Refer to figure 2(a), it can clearly see the homogenous fracture surface, indicating CO plasticiser and MCC particle dispersed uniformly in the PLA matrix. However, for the PEG plasticised sample can see the MCC fibril embedded in the PLA matrix (white arrow) and an aggregate of the MCC (white circle). The poor adhesion allows the explanation of poorer performance in the tensile properties for PLA/MCC/PEG. The previous study by Bijarimi et al. [14] revealed that PEG was dispersed as droplets in the PLA matrix with a clear boundary between the PLA and PEG phases, which led to a reduction in tensile strength.



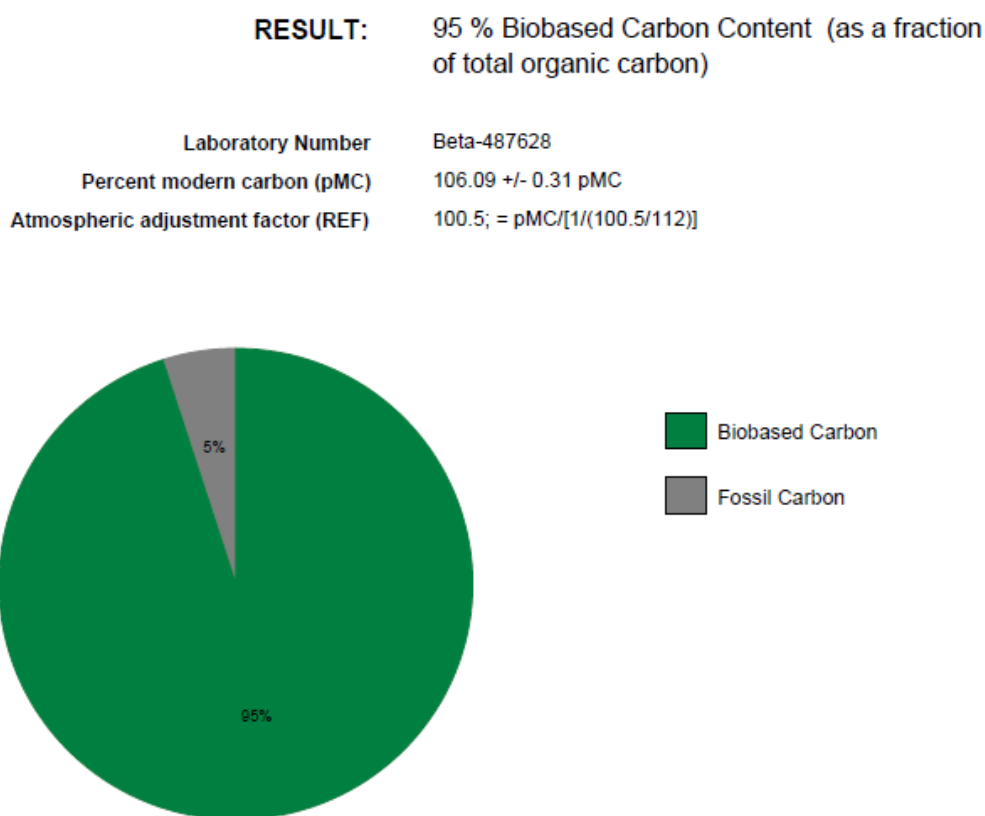
(a)

(b)

Figure 2. SEM fracture surface (a) PLA/MCC/CO (b) PLA/MCC/PEG

3.4. Biobased carbon content

The biobased carbon content for the PLA/MCC/CO was reported as $95 \pm 3\%$ as shown in figure 3. This means of all the organic carbons present in the PLA/MCC/CO, 95% is biobased and 5% is petroleum based. Theoretically, all the 3 components (PLA, MCC, and CO) were derived from plant (i.e., sugar cane, wood pulp, coconut) and supposed to have zero fossil carbon in it. The present of non-renewable carbon ($\sim 5\%$) in the PLA/MCC/CO could be attributed to the impurities during the compounding process or fossil-based chemical used to produce the MCC. Anyway, the biobased content up to 95% was sufficient to certify as a biobased product under the intermediates-plastic resins category as per requirement of U.S. Department of Agriculture (USDA) BioPreferred Program.

**Figure 3.** Biobased carbon content for PLA/MCC/CO

4. Conclusions

Plasticiser CO was better than PEG in providing the plasticity effect on the MCC filled PLA. The CO plasticised sample showed improvement in EB by 12% and recorded higher onset decomposition temperature at 302°C as compared to neat PLA at 290°C . SEM micrograph revealed a homogenous mixture of the PLA/MCC/CO. The PLA/MCC/CO biobased carbon content tested was 95% which was meeting the requirement of USDA to be certified as a biobased product.

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