Effect of Modified Oil on Thermal Properties and Mechanical Properties of Poly(lactic acid) Compressed Sheet

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Abstract

In this study, an eco-friendly plasticizer, i.e. castor oil, was applied with the aim of poly(lactic acid) (PLA) plasticity enhancement. Chemical modification of castor oil was employed in order to improve the effectiveness of plasticization. Effects of the plasticizers on thermal property and mechanical property of PLA compressed sheet were investigated. First, the castor oil was chemically modified by esterification reaction with maleic anhydride. Chemical structure of the successfully modified oil was characterized by FTIR. Then, PLA was compounded with the plasticizers in various contents by using twin-screw extruder. PLA compounded sheet was compression-molded at 2500 psi, 185°C for 8 min. Thermal properties and mechanical properties of PLA compounded sheet were characterized by using differential scanning calorimeter and universal testing machine, respectively. Glass transition temperatures of PLA compounded sheets were decreased with addition of the castor oil either with or without modification. Young's modulus and tensile strength of PLA compounded with the modified castor oil were found to increase with the amount of the additives.

Keywords : Poly(lactic acid), Castor oil, Thermal property, Mechanical Property

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1. Introduction

Poly(lactic acid) (PLA) is one of the most important biodegradable and biocompatible polymer in a group of degradable plastic which can be derived from renewable resources. Due to its excellent properties such as high tensile strength and high modulus, PLA has attracted much attention for the past decades. [1-2] However, it is rigid and brittle at room temperature because of its glass transition temperature (T_g) which is about 60°C. To overcome this limitation, various approaches have been considered including blending with some additives. Plasticization is one effective way to modify physical properties of any polymers. Many plasticizers has been considered and applied to PLA such as glycerol, poly(ethylene glycol), and citrate ester. [3-7] Up to now, various types of plasticizers have still been developed for specific application. [2]

Natural oil is one promising organic compound that may employ as plasticizer since they are inexpensive, nontoxic, and eco-friendly. Moreover, variety of chemical composition makes ease of modification to improve functionality as seen in the example of modified soybean oil which is utilized to improve ductility of poly(vinyl chloride) [8]. Modified castor oil (MACO) is another example of modified oil used as an additive in industrial chemical products, for example, paint [9] and composite material [10], as well as a plasticizer in plastic product such as poly(vinyl acetate) [11] and poly(vinyl chloride) [12].

The chemical structure of MACO consists of long hydrocarbon chains and some modified parts which are derived from maleic anhydride. These hydrophobic and hydrophilic parts make MACO possible to act as a plasticizer in any polymer matrix such as PLA. Moreover, the chemical structure containing ester and carboxylic acid groups may have interaction and assist compatibility with PLA leading to change of PLA properties. So far, there have been a few studies on the utilization of the castor oil as an additive in the PLA product, neither injection molded form nor cast film.

In this present work, we aim to investigate the effect of the modified castor oil on PLA sheet through compression molding process. Thermal and mechanical properties of PLA compounded with unmodified and modified castor oil were compared.

2. Materials and Methods

2.1 Materials

PLA 2002D was supplied by NatureWorks LLC, USA. Castor oil was purchased from Hong Huat Company Limited, Thailand. Maleic anhydride, sodium hydroxide, and anhydrous sodium sulfate were product from Fluka, Switzerland.

2.2 Chemical modification of castor oil

Chemical modification of castor oil with maleic anhydride was adjusted from Wang *et al.*'s mothod [13]. Maleic anhydride (MA) and castor oil (CO) (2.5:1 by mole) were added in a three-neck roundbottom flask equipped with a condenser, a thermometer, and an inlet of dry nitrogen. The reaction proceeded with continuous stirring at 100°C for 8 h. The obtained product was washed by 1M NaOH and distilled water for several times, then dried by using anhydrous sodium sulfate.

2.3 Structural analysis of modified castor oil

Chemical structure of the sample was characterized by Fourier transform infrared spectrophotometric (FTIR) technique. The solid sample (MA) was ground, mixed with KBr, and pressed into pellet whereas the liquid samples (CO and MACO) were placed on a KBr salt disc. FTIR spectra of all compounds were recorded on a Nicolet 6700 spectrometer (Thermo Scientific, USA) in the range 4000-400 cm^{-1} with a 2 cm^{-1} resolution and 32 scans.

2.4 Preparation of PLA compounded sheet

PLA commercial-grade pellets were dried at 60°C overnight before compounding with either CO or MACO in the content of 0.5-5% by weight by using a twin-screw extruder (PRISM TSE 16 TC, Thermo Electron Corporation, UK) at a temperature of 160-170°C and the screw speed 10 rpm. PLA compounded sheet was prepared by using a compression molding machine (LP20, Labtech engineering Co., Ltd., Thailand). PLA compounded pellet was preheated at 185°C for 10 min, compression-molded into sheet in a hydraulic press under a pressure of 17.23 MPa at 185°C for 8 min, and cooled at room temperature.

2.5 Thermal properties of PLA compounded sheet

Thermal analysis was conducted by a differential scanning calorimeter (DSC2910, TA instruments, USA) under a nitrogen atmosphere. The samples (5-10 mg) were hold at 35 °C for 5 min, then heated from 35 to 200 °C at a heating rate of 10 °C/min. Degree of crystallinity (χ_c) was calculated from

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^o} \qquad (1)$$

where ΔH_m and ΔH_c are melting enthalpy and crystallization enthalpy of the samples, respectively, and ΔH_m^o is melting enthalpy of 100% crystalline PLA (135 J/g [14]).

2.6 Mechanical properties of PLA compounded sheet

Tensile properties of the compounded sheets were investigated according to ASTM D882-12 by using universal testing machine (H5K-S, Hounsfield test equipment Ltd., UK) with a 5000 N load cell and a crosshead speed of 20 mm/min. The samples were cut from the compression molded sheets.

3. Results and Discussion

3.1 Chemical modification of castor oil

Molecular structures of MA, CO, and the obtained product were characterized by FTIR. Comparison of FTIR spectra are shown in Fig. 1. MA gives characteristic peaks at 1775 and 1855 cm^{-1} corresponding to anhydride stretching while CO shows peaks at 1745 and 1161 cm^{-1} relating to C=O stretching and C-O stretching in the structure, respectively. After the reaction between MA and CO was carried out, the yellowish transparent liquid was obtained. The product clearly shows the new peaks at 1213 and 1635-1645 cm^{-1} which are corresponding to C-O and C=C stretching, respectively. Moreover, the 1745 cm^{-1} peak which is belonging to C=O stretching shifts to 1739 cm^{-1}. The appearance of C-O and C=C groups as well as the shifting of C=O group in the product spectrum confirm that the esterification reaction between castor oil and maleic anhydride was successful and maleated castor oil (MACO) was obtained. The result was similar to those observed by H.J. Wang *et al.* [13] and C. Mazo et al. [15] Possible reaction between MA and CO is shown in Fig. 2.

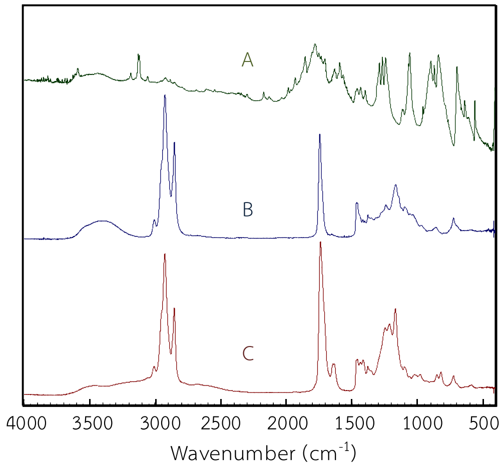

Fig. 1. FTIR spectra of MA (A), CO (B), and the product obtained from reaction between MA and CO (C).

3.2 Thermal properties of PLA compounded sheet

PLA was compounded with either CO or MACO in various ratios. The compound was compressed into sheet by compression molding machine. Effect of the additives on thermal properties of PLA was investigated by DSC. Fig. 3 shows DSC thermograms of PLA, PLA-CO, and PLA-MACO sheets. PLA sheet shows glass transition temperature (T_g), cold-crystallization temperature (T_{cc}) and melt temperature (T_m) at 60.2, 121.1, and 153.8°C, respectively. After adding the additives, both CO and MACO hardly show effect on T_m. However, addition of CO gives T_g decreasing about 1.9 °C. When the amount of CO increases, the T_g decreases. In case of PLA-MACO sheet, T_g of the sheet decreases to 56.9 °C**.** This shows the abilities of CO and MACO which can act as plasticizers.

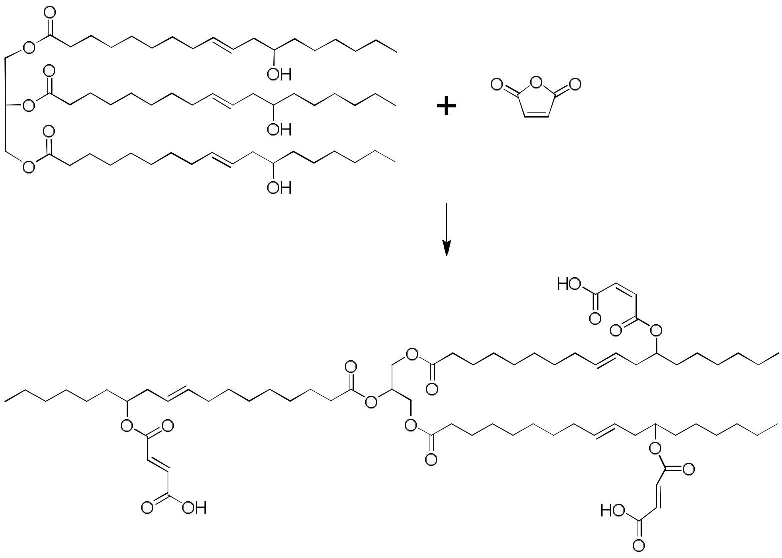

Fig. 2. Possible reaction of CO and MA.

Degree of crystallinity (χ_c) is one factor that is affected from the additives. The pure PLA compressed sheet shows the degree of crystallinity = 1.67%. The values of χ_c were found to decrease to 0.86% and 1.63% when CO was added to 0.5% and 5%, respectively. On the other hand, the PLA-MACO compounded sheet with 5% MACO gives χ_c at 2.52%. This shows that MACO may assist crystallization of PLA.

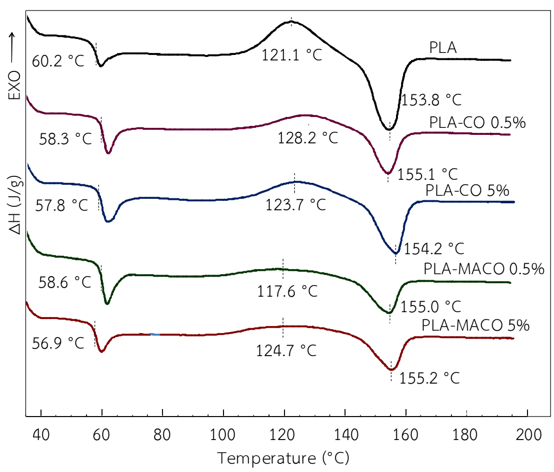

Fig. 3. DSC thermograms of PLA, PLA-CO, and PLA-MACO sheets.

3.3 Mechanical properties of PLA compounded sheet

Not only thermal properties but mechanical properties of the products can be affected by addition of any additives. Tensile properties of PLA compounded sheets were investigated by using universal testing machine.

Fig. 4 shows comparison of Young's modulus of PLA, PLA-CO, and PLA-MACO sheets with various ratios. Young's modulus of PLA sheet is about 323.0 MPa. After addition of CO, Young's modulus increases significantly. But the modulus decreases as the CO content increases. In the case of PLA-MACO sheet, Young's modulus increases gradually with increasing amount of MACO (except 3%). This supports the DSC result which suggested that MACO may help crystallization and affect to the strength of the material.

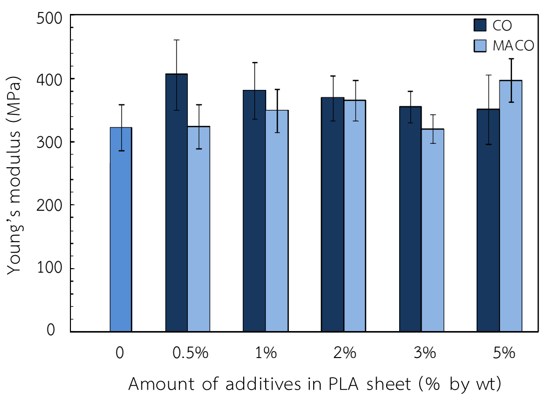

Fig. 4. Young's moduli of PLA, PLA-CO and PLA-MACO sheets.

Tensile strengths of PLA, PLA-CO, and PLA-MACO sheets are shown in Fig. 5. Tensile strength of the pure PLA sheet was found to be about 60 MPa. Adding either CO or MACO decreased the tensile strength of PLA compounded sheets. The reason might be from plasticization ability of CO and MACO similar to the case of poly(vinyl chloride) [12]. However, when the amount of the additive is higher than 2%, the tensile strength of PLA-MACO sheet tends to increase while that of PLA-CO sheet decreases. This might be due to the difference between MACO and CO, i.e. the modified part of MACO which was obtained from maleic anhydride. The aforementioned structure might be able to interact with PLA and induce crystallization in the samples.

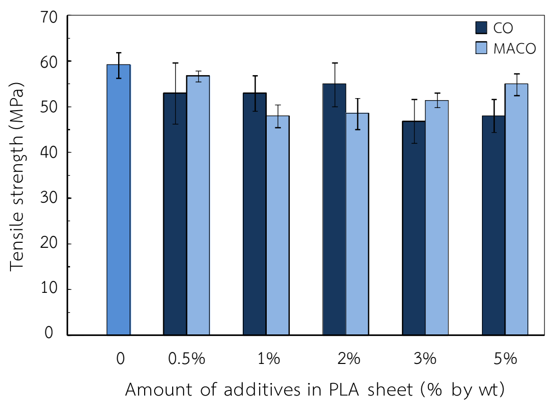

Fig. 5. Tensile strengths of PLA, PLA-CO and PLA-MACO sheets.

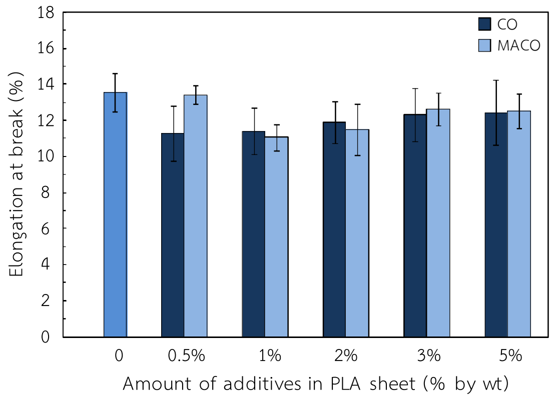

Fig. 6. Elongation at break of PLA, PLA-CO and PLA-MACO sheets.

Elongation at break of the PLA compounded sheet is one factor to be considered. Fig. 6 shows the elongation at break of PLA compressed sheet with various amount of CO and MACO. Addition of CO and MACO decreases the elongation ability of PLA sheet. With increasing amount of the additives, either CO or MACO, the elongation at break of the PLA compounded sheets slightly increases. However, all the values are not much different which might be due to the fluctuation of the samples. This shows that both CO and MACO rarely affect to the plastic deformation.

According to the thermal properties and mechanical properties of the PLA compounded sheets which have been observed, the PLA structure with different amount of CO and MACO may be assumed in Fig. 7. From the result of T_g, both CO and MACO function as the plasticizers. This might be expected that either CO or MACO is possible to penetrate into the PLA structure. That is to say, when the amount of the additive is low, either CO or MACO may disperse in the polymer matrix. With increasing amount of the additives, CO might be aggregated so that decreases in Young's modulus and tensile strength of the compounded sheet were observed. Different from CO, MACO might interact with PLA and induce crystallization of PLA thus the crystallization increases. The strength of polymer is then enhanced.

4. Conclusions

In this study, the modified oil (MACO) was prepared from the esterification reaction between castor oil (CO) and maleic anhydride. MACO and CO were applied in PLA. Thermal properties and mechanical properties of PLA compounded sheets were investigated and compared. Both MACO and CO act as plasticizers as seen in T_g decreasing. However, MACO tends to induce the crystallinity of PLA sheets which corresponds with the increase in Young's modulus observed. Addition of the additives decreases the tensile strength of the PLA sheet at the beginning. However, when a higher amount is added, CO decreases the strength whereas MACO helps increasing of the strength. Considering the properties investigated, PLA with 5wt% MACO was found to be the most efficient compound.

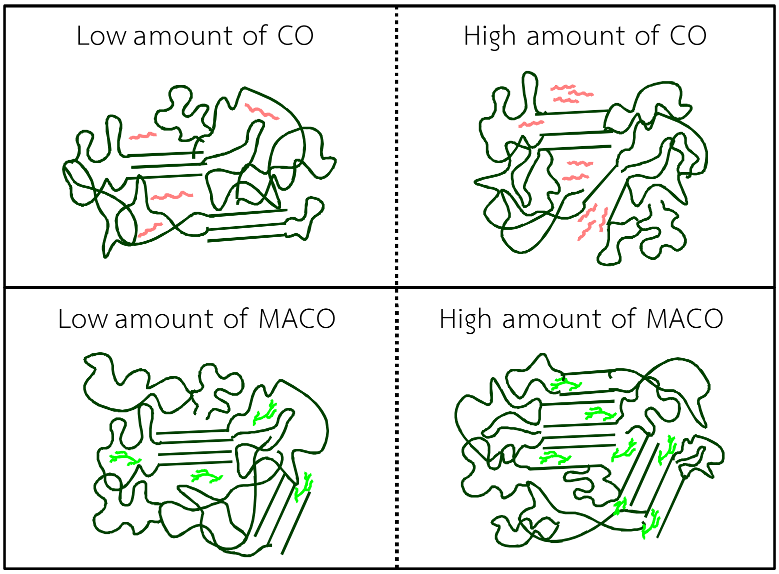

Fig. 7. Schematic diagram explaining the role of the additives (: CO and : MACO) in the PLA matrix.

5. Acknowledgment

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