Grafting of poly (lactic acid) with maleic anhydride using supercritical carbon dioxide

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Abstract. The aim of this work was to modify poly lactic acid (PLA) via free radical grafting with maleic anhydride (MA) by using supercritical carbon dioxide (SCCO₂). Benzoyl peroxide (BPO) was used as an initiator. The solubility of MA in SCCO₂ was first determined to estimate the suitable grafting conditions and equilibrium. From the solubility study of MA in SCCO₂, it was found that the solubility of MA in SCCO₂ increased with the increasing pressure and dissolution time. PLA films were first prepared by compression molding. The ratio of MA to BPO was 2:1. The reaction temperature and pressure were 70°C and 100 bar respectively. The grafting reaction and the degree of grafting were characterized by nuclear magnetic resonance (NMR) spectroscopy and titration, respectively. Scanning electron microscope (SEM) technique and contact angle were used to confirm the changes in physical properties of PLA film grafted MA. NMR spectrum indicated that the grafting of MA onto PLA was successfully achieved. Degree of grafting by using SCCO₂ was as high as 0.98%. This provided rather high grafting degree compared with other processes. SEM pictures showed the rough surface structure on modified PLA film. In addition, contact angle results showed an improvement of the hydrophilicity by maleic anhydride grafting onto polymers.

1. Introduction
Poly (lactic acid) (PLA) is one of the most well-known biodegradable polymers with high mechanical strength and modulus. It is now available largely in a commercial scale and a wide range of products. To expand the application window of PLA, modification on PLA properties has been carried out

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extensively for various applications and purposes. These include the blending of PLA with other polymers, composites and copolymers. The chemical modification of PLA can be performed by grafting desired molecules onto PLA chains in order to improve surface energy of polymer and its hydrophilicity to obtain polymer with suitable functional groups for the benefit of printing and coating applications, adhesion with polar polymers, metal and fibers. Some conventional grafting methods such as radiation [1], melt process [2, 3] and solution method [4] have been reported. However, all these methods have drawbacks, for example, in the melt process, most biodegradable polymers are polyesters and vulnerable to severe thermal degradation during processing [5], thus sacrificing some properties like the mechanical and thermal properties. In the case of the solution process, the removal of organic solvent from the final product is required.

Until recently, the chemical modification of polymer using supercritical fluid, namely supercritical carbon dioxide (SCCO₂), has been explored for many polyolefins due to the ease of using organic solvents and mild processing conditions. High density like liquid and good diffusivity like gas are combined as a powerful solvent. Faster dissolution rate and higher solubility of solutes in supercritical fluid can be achieved. The supercritical fluid most commonly used is carbon dioxide due to its nontoxicity, low-cost, environmental benign, moderate critical conditions (T_c = 31.1 °C, P_c = 7.386 MPa) [6], but low polarity. The polarity of SCCO₂ can be improved using an entrainer, and in many cases ethanol is chosen.

Supercritical carbon dioxide is used in several applications such as separation processing, drug delivery [7, 8], chromatography, synthesis, purification and extraction, providing efficient processes with increased yields and selectivity, as comparable with conventional techniques [9, 10]. Moreover, it can be used for polymerization, polymer processing, plasticizer in polymer system and impregnating agent to make grafted polymer [11]. Grafting chemicals onto polyolefin using SCCO₂ has been carried out by many groups. The major advantage of this method is easy application for polymers in the solid state such as powder, sheet and film. J. H. Hayes and T. J. McCarthy [12] studied free radical grafting of maleic anhydride onto poly(4-methyl-1-pentene) (PMP) film using SCCO₂. It was found that the optimum temperature for the reactions was 125°C, which allowed for rapid reaction without significant sample deformation. In addition, the optimal molar ratio of MA to DCP was found to be 3/2 for optimizing the degree of maleation. T. Liu and his coworkers [13] grafted maleic anhydride onto polypropylene in the solid state by using SCCO₂. The results showed the advantage of using SCCO₂ as an environmentally benign solvent and swelling agent for carrying out the grafting process of malic anhydride onto PP solid state. Moreover, this process produced much higher grafting contents than the conventional melt process did. A Galia and his colleagues [14] modified polypropylene by grafting of MA onto iPP sheet using SCCO₂ method. The result was successfully achieved by controlling the concentration of inorganic peroxide, MA and the density of supercritical fluid. For the modification of PLA, a few investigations have been performed to graft chemicals onto PLA. T. M. Quynh and his coworkers [15] prepared the crosslinked stereo blend of PLLA/PDLA by pretreatment with SCCO₂ with triallyl isocyanurate (TAIC) being used as a crosslinker. The result showed that the brittleness of blend was very much reduced by using SCCO₂. However, after radiation treatments, toughness and tensile strength of blend films can be significantly improved by simultaneous combination of SCCO₂ and radiation treatments.

Therefore, the objective of this work was to modify PLA film by radical grafting with maleic anhydride in SCCO₂. The solubility of MA in SCCO₂ was studied to estimate the suitable grafting condition. Benzoyl peroxide was used as initiator in this work.

2. Experimental

2.1. Materials
Poly (lactic acid) (PLA) 2003D was purchased from NatureWork ® LLC, USA. Maleic anhydride (MA) and benzoyl peroxide (BPO) initiator were purchased from Sigma Aldrich.
2.2. The solubility of MA in SCCO$_2$

To ensure the reaction in supercritical phase, the measurements of solubility of MA at different pressures and dissolution time were required. The solubility of MA in SCCO$_2$ was measured using the set-up of supercritical fluid process as shown in figure 1.

First, the MA (1 g) was placed in the reactor (Re248-D150L230, CHAREON TUT Co., Ltd, Thailand, No. 6 in figure 1). The temperature of reactor was set at 40±1°C. Then the reactor was closed and gradually carbon dioxide was introduced. Carbon dioxide was pumped (No. 3, SITEC, SITEC-Sieber /engineering AG, Switzerland) into the reactor until the desired pressure was reached. The studied pressures were 80, 90 and 100 bars and the dissolution time was varied for 6, 12 and 24 hours. After that, the system fluid was purged slowly. The purged MA in high pressure carbon dioxide was carefully collected with methanol. Then the concentration of MA in methanol was measured by using UV-Vis spectrometer (T80+ UV/Vis spectrometer, PG Instruments Ltd., Bangkok High LAB Co., Ltd) to confirm the results with the gravimetric method. The rest of MA in the reactor was removed from the reactor and then weighted. The solubility of MA in SCCO$_2$ can be calculated from the decrease in MA weight according to equation (1). The amount of carbon dioxide in the reactor was calculated from the known volume and carbon dioxide density. The values of carbon dioxide density were taken from The National Institute of Standards and Technology (NIST) standard reference database [16].

\[
\text{%Solubility} = \frac{\text{Mass of soluble MA}}{\text{Mass of soluble MA} + \text{Mass of CO}_2} \times 100
\]  

(1)

2.3. Grafting reaction in SCCO$_2$

After the measurement of the MA solubility in SCCO$_2$, the suitable condition for grafting reaction was chosen. The film sample was prepared by compression molding (Labtech, LP-S-50, Labtech Engineering Co., Ltd) at 170°C. The film thickness was around 0.2-0.3 mm. The film was cut into the sample of 50x30 mm. Then film sample, with the ratio of MA to BPO being 2/1, was placed in the reactor. The reactor was sealed tightly. The temperature of the reactor was set at 40°C, and then carbon dioxide was filled into the reactor. After that, the temperature was increased to 70°C to allow thermal decomposition of peroxide. Finally, the pressure was increased to the critical point and the reaction was kept for 3 hours. After the reaction, carbon dioxide was vented out. Let the system cool down and the sample was removed from the reactor for further characterizations.

2.4. Characterization and testing
For NMR analysis, PLA grafted MA sample was first dissolved in CDCl₃. The ¹H NMR spectrum was obtained using Bruker Avance 300 NMR Spectrometer.

The graft degree of maleated PLA can be determined by back-titration using phenolphthalein as indicator. First, PLA grafted MA sample was dissolved in chloroform, and then precipitated in methanol to remove the unreacted MA. And 1 g of sample was completely dissolved in 100 ml of chloroform. Then an excess of 0.02 N KOH in ethanol solution was added which made MA thoroughly react after that, 0.02 N HCl in ethanol solution was titrated against KOH. Finally, KOH ethanol solution was added again to the titration end point [17]. Degree of grafting (G%) was calculated from the consumed quantity of KOH, by the following equation:

\[
G\% = \frac{(V_{KOH}N_{KOH} - V_{HCl}N_{HCl} - M_0)}{2W} \times 98.06 \times 100\%
\]  

where \( V \) is the volume (L), \( N \) is the normality (mol/L), \( M_0 \) is the blank value, and \( W \) is the specimen weight (g). The sample was determined for three times and the average degree of grafting was reported.

The morphology of cross section and surface of film samples was investigated by SEM technique. The samples were cooled down in the liquid nitrogen and then fractured. Then, the sample films were rinsed with water to remove the unreacted MA in the sample. They were gold-coated and studied under a working voltage of 15 kV with CamScan, MX 2000 SEM.

As for determining the contact angle determination, the sheet samples were prepared by compression molding (Labtech, LP-S-50, Labtech Engineering Co., Ltd.). The specimens were held on the slide glass and were conditioned at room temperature. Then, water droplets were dripped by a micropipette on the sample surface. The contact angle was measured with Goniometer (Model 200, Rame-Hart Instrument).

3. Results and discussion

3.1. Solubility of maleic anhydride in SCCO₂

The solubility of MA in SCCO₂ at pressures between 80-100 bar was shown in figure 2. To ensure the equilibrium for any constant pressure, the solubility of MA was measured at different dissolution time. It was found that the solubility of MA in SCCO₂ reached the maximum at 24 h for the pressure of 80 and 90 bar whereas at the pressure of 100 bar, the solubility of MA in SCCO₂ did not depend on the dissolution time. The solubility of MA in this pressure range lied between 0.35-0.63%. The pressure of 100 bar was chosen for further experiments due to its highest solvent power and independence of dissolution time.

![Figure 2. The solubility of MA in SCCO₂.](image-url)
When considering the system consisting of peroxide, the decomposition temperature should be taken into account. The decomposition temperature of BPO is at least 70°C with a given half-life time of 92 minutes [18]. Therefore, the reaction temperature should be increased to 70°C, and the dissolution time was then sufficiently reduced to 3 h.

3.2. Characterization of grafted PLA

After reaction, the sample was removed from the reactor and kept in the desiccator at room temperature for 24 h to remove CO₂ residue. The sample was washed with methanol. Then, all samples were characterized by ¹H NMR spectroscopy.

![Figure 3](image)

**Figure 3** ¹H NMR spectrum of PLA grafted with MA in SCCO₂.

From figure 3, a signal at 7.2 ppm was the characteristic of CDCl₃. The signals appeared at 1.2-1.5 and 5.1 ppm corresponded to –CH₃ and –H of PLA, respectively. The succinyl functional groups were generally found in the region of 2-3 ppm [19]. A signal at around 2.6 ppm was assigned to the succinyl group of MA on PLA. The results indicated that graft of MA onto PLA was successfully achieved. However, an weak signal was also observed at around 7.0 ppm which was the characteristic signal of MA [20]. This indicated that there was the residual unreacted MA in sample. However, this problem can be solved by washing film with methanol. The signal at 7.0 ppm disappeared after washing sample film (NMR spectrum was not shown). It indicated that the unreacted MA was removed.

The MA grafting yield was determined by the titration method. The sample was first precipitated to ensure that the unreacted MA was removed. The average degree of grafting of maleated PLA was 0.976 %. It could be seen that grafting by using SCCO₂ provided higher grafting content than that by the solution method [19, 21] and melt method [22]. This may be due to the fact that when the temperature of reaction increased to 70°C, higher than glass transition temperature of PLA (55-60°C), SCCO₂ can swell polymer [14] as well as have powerful solvent for the reaction. Therefore polymer chain had higher mobility and higher free volume as well as became softer. Consequently, this provides high diffusion of MA and BPO into polymer, resulting in the high degree of grafting.

3.3. Morphology of samples

The morphology of the cross section and surface of film samples was characterized by SEM technique as shown in figure 4. Compared with PLA grafted with MA, it was clearly observed that pure PLA film presented a smoother morphology (see figure 4(b)). PLA grafted with MA presented a rougher morphology and some solid crystal particles were impregnated in polymer matrix (see figure 4(d)). These particles sizes were around 10-20 μm which was the same size as MA (the SEM picture of MA crystals was not shown). Thus, this particle might be the MA crystals, which penetrated into the polymer film during the process and then the recrystallization of the finely dispersed MA within the polymer occurred upon reducing the pressure, thus allowing the encapsulation of MA crystals.
result agreed with NMR result as discussed previously. However, the sample film after rinsing with water was also examined and the result showed that a little bit of MA crystal still remained in the film (see figure 4(g)). This could be from the recrystallized MA tightly impregnated in PLA matrix. When considering the surface of the film, it could be seen that the surface of PLA grafted MA sample was rough and wavy (see figure 4(c)) and it became more pronounced in figures 4(e) and 4(h). This result was similar to the work reported by Liu Z. and co-workers [23]. This phenomenon was explained for grafted polypropylene after treating with SCCO$_2$ by the different initiation rates of amorphous and crystalline sites, partly arising from different swelling rates in amorphous and crystalline regions.

![Figure 4 SEM micrographs of cross section of pure PLA film ((a) and (b)), cross section of PLA grafted with MA ((c) and (d)), surface of PLA grafted with MA ((e)), cross section of PLA grafted MA film after rinse ((f) and (g)) and surface of PLA grafted with MA after rinse ((h)).](image)

3.4. Water contact angle

The average values of contact angle for pure PLA film and PLA grafted with MA were shown in table 1.

| Sample                      | Contact angle (°) |
|-----------------------------|-------------------|
| Pure PLA film               | 100.1             |
| PLA grafted with MA         | 86.1              |

It was observed that the contact angle of polymers grafted with MA was lower compared with pure polymers. The decrease in contact angle was mainly ascribed to the modified surface of polymer films as shown in SEM results and it corresponded to the improvement of the hydrophilicity by maleic anhydride grafted onto polymers. This result was in good agreement with the work of D. Muenprasat.
and her coworkers that modified PLA with maleic anhydride through free radical solution reaction can improve the hydrophilic property of PLA [24].

4. Conclusion
The modification of PLA film by free radical grafting with MA is successfully prepared in SCCO$_2$. Pressure of CO$_2$ and the dissolution time affect the solubility of MA in SCCO$_2$. Thus, the reaction is carried out at 100 bar with 3 h reaction time for effective grafting reaction. The average degree of grafting is 0.976 %, which is relatively high compared with both solution and melt processes. The high grafting degree is required for tailoring most of the hydrophobic biodegradable polymers. In addition, PLA film grafted with MA shows better hydrophilicity as confirmed by contact angle. In terms of industrial production, the easy-to-setup supercritical fluid technology and high effectiveness are very attractive and can provide alternatives and versatile products. For the further work, the modification of as-received PLA resin will be conducted together with the elucidation of the relationship between molecular weight and the loading concentration of peroxides.

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