Relationship between compatibilizer and yield strength of PLA/PP Blend

Pattanun Jariyakulsith¹ and Somchai Puajindanetr²
¹,² Department of Industrial Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

¹ploy_pattanun@hotmail.com, ²fiespj@hotmail.com

Abstract. The aim of this research is to study the relationship between compatibilizer and yield strength of polylactic acid (PLA) and polypropylene (PP) blend. The PLA is blended with PP (PLA/PP) at the ratios of 70/30, 50/50 and 30/70. In addition, (1) polypropylene grafted maleic anhydride (PP-g-MAH) as a compatibilizer at 0.3 and 0.7 part per hundred of PLA/PP resin (phr) and (2) dicumyl peroxide (DCP) being an initiator at 0.03 and 0.07 phr are added in each composition. Yield strength is characterized to study the interaction between compatibilizer, initiator and yield strength by using experimental design of multilevel full factorial. The results show that (1) the yield strength of PLA/PP blend are increased after addition of compatibilizer. Because the adding of PP-g-MAH and DCP resulted in improving compatibility between PLA and PP. (2) there are interaction between PP-g-MAH and DCP that have affected the final properties of PLA/PP blend. The highest yield strength of 27.68 MPa is provided at the ratio of 70/30 blend by using the 0.3 phr of PP-g-MAH and 0.03 phr of DCP. Linear regression model is fitted and follow the assumptions of normal distribution.

1. Introduction
The number of plastic waste increases in recent years. To concern the environmental impact, the biodegradable materials are play in a crucial role in daily life. Thus, this research interested in biodegradable polymer called polylactic acid (PLA) which is derived from the starch or sugar cane [1,2]. PLA widely used especially in disposable packaging materials such as bags, food packaging, home appliances and compostable tableware, because of its good mechanical properties [2-4]. However, the limitations of PLA are rigid and brittle at room temperature [2,4], so its applicability has been limited. PLA might be improved by using the techniques such as melt blending with tough polymers, plasticization, and chemical modification [3]. Hence, PLA which was blended with soft and tough polymers can lead to enhance mechanical properties and biodegradability [4]. Polypropylene (PP) is a commodity polymer with worldwide production, low cost, easiness of processing and non-toxicity [5]. However, the properties of polymer blend are limited because of the limited compatibility between phases of polymers. To solve this problem by enhancing the adhesion between phases, the compatibilizers are often used as additives [6]. Polypropylene grafted maleic anhydride (PP-g-MAH) is well known as an effective compatibilizer for blending PP with polar polymers (i.e. PLA). Maleic anhydride is a famous initiator because of chemically good react with the PLA, availability, low toxicity and low potential to react in itself during the process [7]. Some paper was studied about effect of PP-g-MAH as a compatibilizer on PLA/PP blend, the morphology analysis of PLA/PP blend confirmed that filling of PP-g-MAH can lead to adhesion between PLA and PP. From the Scanning Electron Microscopy of PLA with PP-g-MAH, showed the ductile fracture due to interaction of PP-g-MAH and...
PLA [5]. For more details, the study of mechanism of melt grafting observed that the amount of maleic anhydride correlated with the level of DCP which effect to the properties [8]. Another research used the PP-g-MAH to improve the compatibility of PLA/PP blend, confirmed that PP-g-MAH was coupled with PP by the PP part in its molecule and the anhydride part reacted with the polar part in PLA molecule. Furthermore, it can be seen that the PLA improved the biodegradability of PP [9]. So the PLA/PP blend would become a new alternative to be a biodegradable materials. To define all the factors that effect on desirable properties in order to reduce cost, production time, even the optimal condition of processing, the experimental design should be involved. This research aimed to improve the mechanical properties of PLA by blended with PP in order to approach the new material that degradable, good mechanical properties and the lowering cost simultaneously. To study the relationship between the PP-g-MAH as a compatibilizer and DCP as an initiator to the properties of PLA/PP blend which under the ratios of 70/30, 50/50 and 30/70 by using the experimental design method. In addition, (1) PP-g-MAH at 0.3 and 0.7 phr and (2) DCP at 0.03 and 0.07 phr were added in each composition. Yield strength are investigated. For the future, PLA could formed by various polymer processing and could have more applications without the limitations.

2. Materials and methods

2.1. Materials
Polyactic acid (PLA) resin, 4032D grade (available in pellet form) was purchased from NatureWorks LLC. Polypropylene resin, HP6060 grade were supplied by HMC polymers. Polypropylene grafted maleic anhydride (PP-g-MAH) was purchased from Sigma-Aldrich as a compatibilizer. Dicumyl peroxide (DCP), supplied by Kit Phaibun Chemistry Ltd, was used as an initiator.

2.2. Preparation of blending of PLA/PP
The Blending of PLA/PP using the extrusion via twin screw extruder, with/without initiator and compatibilizer. The conditions for twin screw extruder were as follows: (1) Screw speed at 40 rpm, (2) Temperature of 10 zones were (175/180/190/190/195/195/195/195/180/180°C respectively). In addition, the pellets of polymers were dried all night at 55 °C before processing. The PLA/PP blend was carried out by extruder, then compressed to be the specimen by compression moulding at 200 °C, pre heating for 20 minutes, and pressure of 1.96 MPa for 5 minutes.

2.3. Testing and characterization
Yield strength were tested according to ISO527-2 by tensile testing machine as a model of 112.100kN.H. from MMT engineering co., ltd. The conditions of testing were as follows: (1) cross head speed of 5 mm/min and (2) load cell of 100kN.

2.4. Experimental design
As mentioned above, the proper amount of compatibilizer is an important point to consider, because it would effect on the final properties of polymer blend. Therefore, the experimental design would play a role which can reach about interaction between factors and responses with precise estimation in main effects of each factor and their interactions. In this study selected multilevel full factorial design using the Minitab17 with random of five replicates and the levels of factors are shown in table 1.
Table 1. Factors and levels for experimental design

| Factors         | Levels |
|-----------------|--------|
|                 | Low    | Medium | High  |
| Factor A : PLA (%) | 30     | 50     | 70    |
| Factor B : PP-g-MAH (phr) | 0.3   | -      | 0.7   |
| Factor C : DCP (phr)  | 0.03   | -      | 0.07  |

*part per hundred of PLA/PP resin

3. Results and discussions

3.1. Analysis of variance

To understand the significant of factor to yield strength, the analysis of variance from Minitab 17 was used which shown in figure 1.

| Source            | DF  | Adj SS  | Adj MS  | F-Value | P-Value |
|-------------------|-----|---------|---------|---------|---------|
| Regression        | 9   | 748.427 | 83.158  | 28.53   | 0.000   |
| PLA               | 1   | 14.600  | 14.599  | 5.01    | 0.030   |
| PP-g-MAH          | 1   | 0.153   | 0.152   | 0.05    | 0.820   |
| DCP               | 1   | 19.316  | 19.3163 | 6.63    | 0.013   |
| PLA*PLA           | 1   | 55.972  | 55.971  | 19.20   | 0.000   |
| PLA*PP-g-MAH      | 1   | 2.889   | 2.8888  | 0.99    | 0.324   |
| PLA*DCP           | 1   | 64.579  | 64.5790 | 22.15   | 0.000   |
| PP-g-MAH*DCP      | 1   | 26.215  | 26.2149 | 8.99    | 0.004   |
| PLA*PLA*PP-g-MAH  | 1   | 20.783  | 20.7834 | 7.13    | 0.010   |
| PLA*PP-g-MAH*DCP  | 1   | 76.121  | 76.1208 | 26.11   | 0.000   |
| Error             | 50  | 145.747 | 2.9149  |         |         |
| Lack-of-Fit       | 2   | 3.273   | 1.6365  | 0.55    | 0.580   |
| Pure Error        | 48  | 142.474 | 2.9682  |         |         |
| Total             | 59  | 894.174 |         |         |         |

Figure 1. Analysis of variance

From the figure 1, can conclude that there are two types of significant factor (p-value < 0.05) which consist of (1) main effects; the content of PLA and content of DCP. And (2) interaction effects that are interaction between PLA/DCP and interaction between PP-g-MAH/DCP. All of these factors are significantly affect to the yield strength of PLA/PP blend.

3.2. Main & interaction effects

To understand the relationship between compatibilizer and yield strength, the Minitab 17 is needed. Because some factor is not directly affect the yield strength but it might influence under interaction with another factor. So in this research will describe by the main effect plot and interaction plot which are shown in figure 2 to easily understand.
Figure 2. (a) main effects plot, (b) interaction effects plot for yield strength.

As the figure 2(a) and 2(b) show main effects plot and interaction effects plot for yield strength respectively. In main effects plot describe that the yield strength are changed when the content of PLA increases and show the enormous changing from medium to high level of PLA. The addition of only PP-g-MAH seems not to affect the yield strength, it need to be used with another factor to notice the different. In the contrary, the increasing of DCP responsible for the yield strength to decrease. For the interactions plot, shows the interaction between PLA and PP-g-MAH are as follows: (1) at the high level of PLA, if add the PP-g-MAH can lead to the reducing of yield strength while (2) addition of PP-g-MAH at low level and medium level of PLA causes gradually increase in yield strength. Next, the interaction between PLA and DCP which effects to yield strength can describe as follows: (1) at high level and low level of PLA, increasing in DCP can lightly effect on yield strength in negative way. Conversely, (2) filling of DCP bring about the yield strength to be higher at the medium level of PLA. And the last is interaction between PP-g-MAH and DCP are reversely effect to the yield strength, it means that changing from low level to high level of DCP at the low level of PP-g-MAH provides the yield strength to be poor, while at the high amount of PP-g-MAH with increasing in DCP gives the raising of yield strength.

3.3. yield strength in each composition

In the figure 3 as below, it can be seen that, the greater amount of DCP at 0.3 phr of PP-g-MAH in each composition can result in the lower yield strength. It may be concluded that the excessive amount of DCP can lead to the overwhelming of free radicals in blending, then induced the chain of polymer to entangle as a result of diminished yield strength. On the contrary, the changing of DCP from low to high level at constant 0.7 phr of PP-g-MAH can lead to the higher yield strength. Because at the more amount of PP-g-MAH which means there is some remained of PP-g-MAH in reaction, so the free radicals from DCP can react with PP-g-MAH, PLA and PP. In addition, each composition of PLA/PP blend can summarize into two cases as follow; (1) at the ratio 30/70 and 70/30 of PLA/PP, using the 0.3 phr of PP-g-MAH and 0.03 phr of DCP will provide the highest yield strength but (2) at ratio of 50/50 of PLA/PP, using 0.7 phr of PP-g-MAH and 0.07 phr of DCP gives the highest yield strength. It may conclude that at the different ratio of polymer, the optimal content of used compatibilizer and initiator would not be the same amount. Thus, approaching the optimal solution by using the experimental design will be useful in the future.
3.4. Regression model

For develop the effective model, the normal probability plots of residual for yield strength follows the assumption of normal distribution and the variances are at constant. In this study, $R^2$ (%) and regression model of yield strength is shown in table 2. It reveals the $R^2$ are closer to 100%, so this model is an effective tool to predict the mechanical properties as a requirement in commercial industry.

Table 2. Regression reduced model for response.

| Response                  | Regression reduced model*                           | $R^2$ (%) |
|---------------------------|----------------------------------------------------|-----------|
| Yield strength (MPa)      | $Yield \text{ strength} = 27.27 - 0.738A - 3.7B + 246.0C$  
                          | $+ 0.01379 A^2 + 0.609AB - 8.55AC – 532BC$  
                          | $- 0.01561 A^2B + 17.24ABC$            | 83.70     |

* A,B,C are the factors in table 1

From the regression model, can conclude that the decreased of one phr in PLA leads to reduce the 0.738 MPa of yield strength and also in PP-g-MAH that decreased of one phr responsible for declined 3.7 MPa of yield strength. In the other hand, the adding of one phr of DCP results in the higher of yield strength to 246 MPa. Not only the main effect but also the interaction effect that influence to the yield strength as shown in the model.

4. Conclusion

The investigation of this study provide the regression model that fitted the data and resulting in the effective forecast to mechanical properties which can practical in production with the required properties. From this study, the improvement of yield strength depends on the amount of compatibilizer, initiator and interaction between them. From overall of the results, the yield strength of PLA/PP blend are improved after adding the compatibilizer which result from enhancing the adhesion between phases as shown in figure 4. PLA/PP blend (70/30) with 0.3 phr PP-g-MAH and DCP 0.03 phr has the highest yield strength of 27.68 MPa. However, the tough and soft polymer may act as a plasticizer in the blending of polymer, so addition of plasticizer more than 20-30% into PLA matrix can cause the phase between polymer blend to separate [2]. Hence, the changing of properties could not clearly distinguishable.
Figure 4. Yield strength of PLA/PP blend with and without PP-g-MAH and DCP

References

[1] Detyothin, S., Selke, S.E.M., Narayan, R., Rubino, M. and Auras, R. (2013) Reactive functionalization of poly(lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA. *Polymer Degradation and Stability*, 98(12), 2697-2708.

[2] Hassouna, F., Raquez, J.M., Addiego, F., Dubois, P., Toniazzo, V. and Ruch, D. (2011) New approach on the development of plasticized polylactide (PLA): Grafting of poly(ethylene glycol) (PEG) via reactive extrusion. European Polymer Journal, 47, 2134-2144. Wit, E. and McClure, J. (2004) Statistics for Microarrays: Design, Analysis, and Inference. 5th Edition, John Wiley & Sons Ltd., Chichester.

[3] Ku Marsilla, K.I. and Verbeek, C.J.R. (2015) Modification of poly(lactic acid) using itaconic anhydride by reactive extrusion. *European Polymer Journal*, 67, 213-223. Giambastiani, B.M.S. (2007) Evoluzione Idrologica ed Idrogeologica Della Pineta di San Vitale (Ravenna). Ph.D. Thesis, Bologna University, Bologna.

[4] Hamd, K., Kaseem, M. and Deri, F. (2012) Poly(lactic acid)/low density polyethylene polymer blends: preparation and characterization. *ASIA-PACIFIC JOURNAL OF CHEMICAL ENGINEERING*, 7, 310-316.

[5] Pivsa-Art, S., Kord-Sa-Ard, J., Pivsa-Art, W., Wongpajan, R., O-Charoen, N., Pavasupree, S. and Hamada, H. (2016) Effect of Compatibilizer on PLA/PP Blend for Injection Molding. *Energy Procedia*, 89, 353-360.

[6] Ebadi-Dehaghani, H., Khouakdar, H.A., Barikani, M. and Jafari, S.H. (2015) Experimental and theoretical analyses of mechanical properties of PP/PLA/clay nanocomposites. Composites Part B: Engineering, 69, 133-144.

[7] Hwang, S.W., Lee, S.B., Lee, C.K., Lee, J.Y., Shim, J.K., Selke, S.E.M., Soto-Valdez, H., Matuana, L., Rubino, M. and Auras, R. (2012) Grafting of maleic anhydride on poly(L-lactic acid). Effects on physical and mechanical properties. *Polymer Testing*, 31(2), 333-344.

[8] Shi, D., Yang, J., Yao, Z., Wang, Y., Huang, H., Jing, W., Yin, J. and Costa, G. (2001) Functionalization of isotactic polypropylene with maleic anhydride by reactive extrusion: mechanism of melt grafting. *Polymer*, 42(13), 5549-5557.

[9] Ploypetchara, N., Suppakul, P., Atong, D. and Pechyen, C. (2014) Blend of Polypropylene/Poly(lactic acid) for Medical Packaging Application: Physicochemical, Thermal, Mechanical, and Barrier Properties. *Energy Procedia*, 56, 201-210