

IDENTIFICATION OF MAXIMUM MELT BLEND RATIO FOR POLYLACTIDE/POLYBUTYLENE SUCCINATE BASED ON RHEOLOGICAL MODEL

Suwan Aekram, Natphichon Budtri, and Weerasak Lertsiriyothin*

Received: October 17, 2021; Revised: November 23, 2021; Accepted: February 28, 2022

Abstract

Rheological model of the polylactide (PLA)/polybutylene succinate (PBS) blend as a function of shear rate, temperature and PBS content was proposed for predicting the shear viscosity of PLA/PBS blends. Melt blending of PLA/PBS with various ratios was prepared by using a single screw extruder and a disk shape sample required for rheological measurement was obtained by a compression molding process. Effect of PBS content on the compatibility of the blend was thoroughly investigated via rheological behavior. The results of rheological properties indicated that below 35% of PBS, The steady shear rate testing of the blends over the shear rate of 0-1,000 s⁻¹ exhibited the shear-thinning non-Newtonian behavior. The shear viscosity of the PLA/PBS blends as a function of shear rate, softening temperature and %PBS content was able to predict from the modified Cross model. Moreover, each blending ratio contained individual set of zero shear viscosity and infinite shear viscosity indicating a profound impact of PBS on the flow behavior of the blend and partial miscibility of the melt blend process.

Keywords: Polylactide (PLA), Polybutylene succinate (PBS), Rheological model

Introduction

Recently, studies on biodegradable polymeric materials have become the main research for industry since the biodegradable materials can replace petroleum-based polymers which are causing serious global environmental waste pollution. PLA is a linear thermoplastic polyester having good mechanical, excellent flavor barrier and biodegradable properties (Fang and Hanna 1999). However, other processing-related properties such as melt viscosity, flexibility, impact strength, and brittleness are not good enough for packaging application (Ogata *et al.*, 1997). Therefore, improving

PLA properties with various techniques have been widely investigated. Blending of PLA with other polymers was one of the common techniques reported to greatly alter its physical properties while blending phase could be controlled in the acceptable miscibility level, for example, mixing with polyvinyl acetate (Gajria *et al.*, 1996), polyethylene glycol (Sheth *et al.*, 1997), polybutylene succinate (Bhatia *et al.*, 2007), poly(butylene terephthalate) (PBT) (Yokohara *et al.*, 2011), poly(carbonate) of bisphenol A (PC) (Phuong *et al.*, 2014) and poly(butylene succinate)-co-adipate (PBSA)

School of Agricultural Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand. E-mail: aekrum@gmail.com

* Corresponding author

and poly[(butylene adipate)-co-terephthalate (PBAT) (Nofar *et al.*, 2015).

In this study, compounding of PLA to improve its processability and certain mechanical properties, specifically in term of melt flow properties, flexibility and resiliency was the main objective.

Polybutylene succinate (PBS) was chosen to blend with PLA since PBS had high flexibility, excellent impact strength, thermal, chemical resistance and processability (Bhatia *et al.* 2007). The impact of PBS blending quantity on the flow behavior of plastic was thoroughly investigated via rheological testing and shear viscosity modeling of the compounds was also the focus. The model was known to be useful in engineering applications that relate to the proper design and optimization of the polymer processing as well as for the understanding of the transport processes (Rao *et al.*, 1997).

Materials and Methods

Materials

An extrusion and thermoforming grade of PLA (code 2002D) was purchased from NatureWorks in pellet form. PBS used in this study is GS Pla (code AZ91TN with a melt index of 4.5 g/10min) from Mitsubishi Chemical (Thailand) Co., Ltd., and produced by DIA Chemical Co., Ltd.

Compounding Process

PLA and PBS resins were dried in vacuum oven (Heraeus Instrument, Model Vacuthem, Heraeus Group, Hanau, Germany) at a temperature of 60°C for 4 h to remove moisture content before processing. Melt blending process was performed by a single screw extruder (Betol, Model BC32, Betol Machinery Ltd., England) Since main target of this work is to define the maximum blending ratio and the PBS effect on rheological behavior, unusual high level of polymer melt blend ratio was purposely predetermined as appeared in Table 1.

Table 1. Composition ratio of PLA(2002D)/PBS blends

PLA (% by mass)	PBS (% by mass)	Compound name
100	0	PLA100/PBS0
80	20	PLA80/PBS20
65	35	PLA65/PBS35
50	50	PLA50/PBS50
0	100	PLA0/PBS100

Rheological Measurement

For rheological measurement, disk shape (diameter = 25 mm and thickness = 1 mm) was prepared from the PLA/PBS blends via hot pressing at 160°C. The rheological properties of the blend

compounds were measured by AR-G2 Rheometer (TA Instruments Ltd., Surrey, England) with parallel plate geometry of 25 mm diameter and gap geometry 0.8000 mm. The following rheological measurements were carried out.

a) Dynamic strain sweep testing over 0.01-100 %strain to confirm the linearity of viscoelastic region.

b) Dynamic frequency sweep testing over frequency range of 0.01-100 rad.s⁻¹ at temperature of 160-190°C.

c) Steady shear rate testing to characterize the flow: The testing covered the shear rate of 0-1,000 s⁻¹ at four temperatures (160°C, 170°C, 180°C, 190°C).

Rheological parameters were directly obtained using the manufacturer supplied computer software (Rheology Advantage Data Analysis Program, TA Instrument).

The maximum blending ratio of the PLA/PBS without phase separation can be interpreted from the rheological properties obtaining by the dynamic frequency sweep testing. The interpretation of rheological properties must be carried out at the same material flowing state that is notified by the angular frequency range showing relatively constant delta value. The delta value represents the phase shift between dynamic viscosity and loss viscosity or storage modulus and loss modulus, therefore any deviation of the delta value is an indication of different flowing state or molten state in its microstructure. To acquire the effect of blending ratio on the phase separation, time-temperature superposition concept of the complex viscosity was applied to dynamic frequency sweep testing data of four temperatures. In the complex plane, a single circular arc of the Cole-Cole plot indicates a homogeneous phase of polymer blend (Vernay and Michel 1985; Wisniewski *et al.*, 1985). This representation can be written as in Equation (1).

$$\eta^* = \frac{\eta_0}{1 + (j\omega\tau)^{1-h}} \quad (1)$$

where η^* is the complex shear viscosity, η_0 is zero shear viscosity, τ is characteristic time, ω is frequency and h is the parameter that characterizes the width of the relaxation time distribution. This representation will be used for characterization of the phase separation behavior of PLA/PBS blends.

Rheological Modelling

The flow behavior of PLA/PBS blends at a given temperature, mass fraction of PBS and shear rate was interpreted and their effects on the shear viscosity were modeled. Pre-existing viscosity

models of the polymer melt were challenged to the measured data and the best model was suggested for PLA/PBS melt blend. All model parameters were obtained by a nonlinear regression method for two variables.

Results and Discussion

Rheological Behavior

Preliminary studies were conducted on neat polymer and all the PLA/PBS blending ratios to ensure that the dynamic properties were measured in the linear viscoelastic region. Dynamic strain sweep testing was firstly checked to ensure the linear viscoelastic region of the material before performing dynamic frequency sweep testing. Linear viscoelastic region tells that within this region the configuration of the macromolecules remains unperturbed by the flow history. On the other hand, microstructure of the material would not be destroyed by shear alignment during the testing. For the dynamic strain sweep testing at a constant frequency of 1 rad.s^{-1} and a constant temperature of 170°C , it was observed that neat polymer and all blending ratios showed linear viscoelastic behavior, relatively constant storage modulus (G'), within the %strain range of 0.03 to 20 (Figure 1). Therefore, the constant strain of 1% was set for dynamic frequency sweep testing over frequency range of $0.01\text{--}100 \text{ rad.s}^{-1}$ in order to evaluate the melt blending characteristic of PLA/PBS based on linearly viscoelastic property.

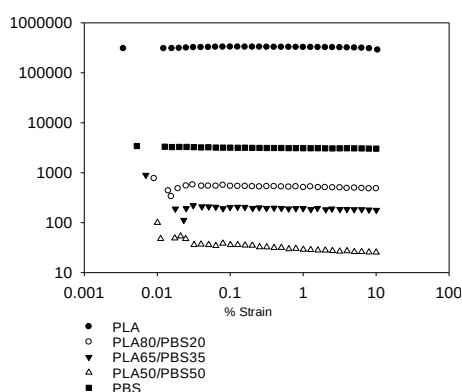


Figure 1. Storage modulus as a function of %strain at 170°C and a constant frequency of 1 rad.s^{-1} for neat PLA, PBS and PLA/PBS blends

In order to apply the time-temperature superposition concept in evaluation the effect of blending ratio on the phase separation, the viscoelastic properties must be obtained under the dynamic frequency sweep testing for a set of

temperature. Generally, the testing temperature is commonly set to cover quite a wide range of polymer processing temperature if anyone wants to evaluate the potential scenario for phase separation. Therefore, the linear viscoelastic region is not the only criteria for the interpretation of the viscoelastic properties, but also all the viscoelastic data must be carefully compared while all of the testing materials are under the flowing state during analysis. Technically, the raw data of viscoelastic properties at a wide range of testing temperature seems not possible to get the similar flowing state, however the relative form of data is the other way to allow us to compare the viscoelastic at the same flowing state.

Here, the linear viscoelastic response within the similar flowing state for the dynamic frequency sweep testing of various temperature can be determined by a linear relation of storage modulus (G') and loss modulus (G''). In Figure 2, we found that PLA has the linear and superimpose viscoelastic properties for all testing temperatures ($160, 170, 180, \text{ and } 190^\circ\text{C}$) in the frequency range of $0.6\text{--}100 \text{ rad.s}^{-1}$. However, the deviation from the linearity of $G'(G'')$ was shown for all the testing temperature of the frequency below 0.6 rad.s^{-1} and at the lowest testing temperature of 160°C , the viscoelastic properties was not in superimposition with other higher melt temperature.

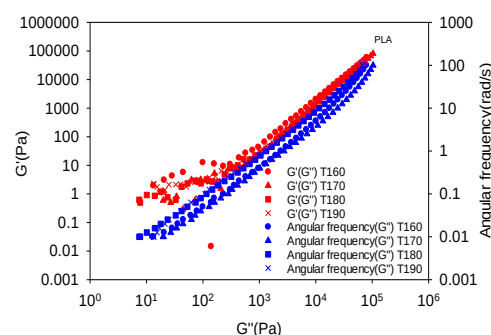


Figure 2. Storage modulus (G') and angular frequency (ω) as a function of loss modulus (G'') of PLA

The non-superimposition suggested that PLA was not in the similar flowing state at 160°C comparing to other temperatures since this temperature was far below the melting temperature of PLA. In addition, we often observed the fluctuation characteristic of the viscoelastic properties in the low frequency range (below 0.6 rad.s^{-1}) even if a relatively short equilibrated time interval of 1 sec for frequency sweep was already set. It should be noted here that the rheometer (AR2 system) is programmed to recursively check every 1 sec until reaching the steady state for each frequency. On the

other hand, the measuring time for frequency below 1 rad.s^{-1} was usually taken a much longer time than 1 sec between any two consecutive frequencies in order to reach equilibrium or steady state. It was due to these facts, the dynamic frequency sweep testing within $160\text{--}180^\circ\text{C}$ for PLA did not provide us the plateau complex viscosity toward the lower frequency between $0.1\text{--}0.6 \text{ rad.s}^{-1}$, so the Cox-Merz rule was not applicable. Unlike PLA, the dynamic frequency sweep testing at all the testing temperatures (160°C , 170°C , 180°C , and 190°C) for PBS, the molten state of PBS appeared to be in the similar flowing state of all testing temperatures since its melting temperature of 115°C was much lower than the testing temperature. Results for Figure 3 showed that the viscoelastic properties were superimposed for all testing temperatures within the linear viscoelastic region or in the frequency range of $0.5\text{--}100 \text{ rad.s}^{-1}$.

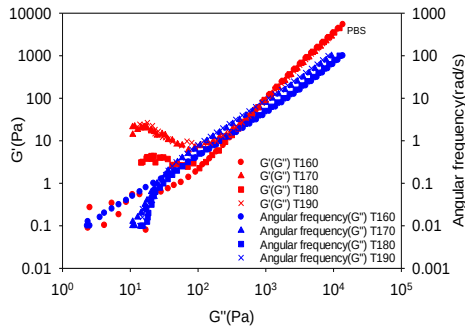


Figure 3. Storage modulus (G') and angular frequency (ω) as a function of loss modulus (G'') of PBS

In addition, the fluctuation characteristic of viscoelastic properties was still noticeable toward very low frequency (below 0.06 rad.s^{-1}), especially at 160°C . Even though the plateau shape of $G'(G'')$ for PBS was somewhat obtained in the very low frequency, the predictive viscoelastic properties at the lowest frequency may be unreliable due to the influence of non-linear viscoelastic characteristics. To be able to evaluate the phase separation of the PLA/PBS blend base on the rheological data covering a wide range the process temperature, a relative form of viscoelastic data in such a way that all data were strictly in a similar flowing state was suggested in the next section.

To evaluate the phase separation in a molten state of the blend compounds, the principle of temperature invariant characteristics of viscoelastic properties was employed. The transition from homogeneous state to heterogeneous state could be indicated by violation of temperature superposition characteristic of viscoelastic properties (Collyer and

Clegg 1998). Here, the modified Cole-Cole plot, appearing in the relative form, was proposed by taking the normalization concept as reported by Vinogradov and Malkin (1980) and Shumsky *et al.* (2010). Original concept, the temperature invariant characteristic of viscoelastic properties may be obtained if the viscoelastic properties as a function of dynamic frequency sweep were divided by zero shear viscosity, for example, a plot of $\eta^*(\omega)/\eta_0$ versus $\omega\eta_0$ and $\eta''(\omega)/\eta_0$ versus $\eta'(\omega)/\eta_0$ etc. The zero-shear viscosity was normally assumed as an equivalent of the complex viscosity at the lowest angular frequency (or at loss modulus (G'') = 0) based on the Cox-Merz rule, so it was indeed implied for truly measurable the zero shear viscosity. However, the dynamic frequency sweep testing covering a wide range of process temperature has often provided data with either unreachable zero shear viscosity due to the detection limit of the instrument at low frequency or the potential fluctuation of data toward the very low frequency as a result of material in different flowing state. The impact of both rational on the measured values of complex viscosity at very low angular frequency was expressed in Figures 4 and 5, so it prevented us to assume the complex viscosity at the

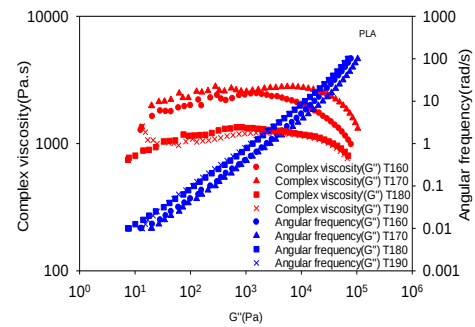


Figure 4. Complex viscosity and angular frequency as a function of loss modulus at all testing temperature for neat PLA

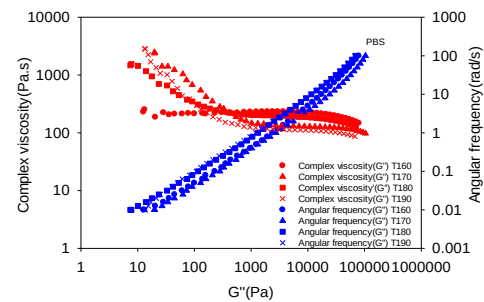


Figure 5. Complex viscosity and angular frequency as a function of loss modulus at all testing temperature for neat PBS

lowest angular frequency equivalent of the zero-shear viscosity.

Instead of using η_0 as a normalized factor, we proposed to present the viscoelastic properties in a relative form or divided the data by the reference complex viscosity $\eta_{ref}^*(\omega)$. The reference viscosity was determined in the linear region of $\eta^*(G'')$ which the materials have a similar flowing state. Here, the reference viscosity, $\eta_{ref}^*(\omega)$, for each blending ratio was a complex viscosity ($\eta^*(\omega)$) at the least minimum value of the loss viscosity $\eta''(\omega)$ in the Cole-Cole plot which represented the transition of different flowing state at a given constant temperature as an example shown in Figures 6 and 7.

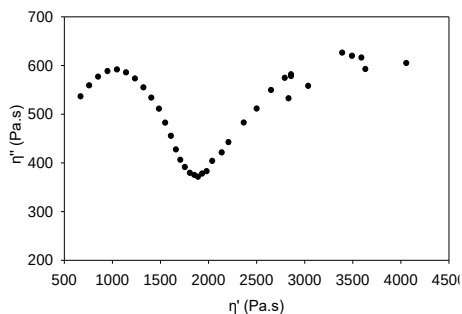


Figure 6. Cole-Cole of PLA80/PBS20 blend at 160°C

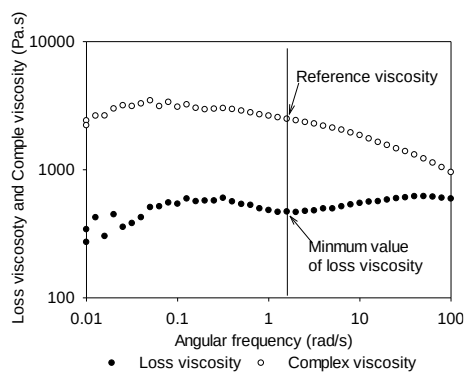


Figure 7. Loss viscosity and Complex viscosity as a function of angular frequency at 160°C to determine the reference viscosity at minimum loss viscosity for PLA80/PBS20 blend

The dynamic frequency sweep testing was conducted at 160, 170, 180, and 190°C under 1% strain amplitude which was in the linear viscoelastic regions. Since a wide range of blending ratio of PLA and PBS (from 20% to 50%) and great different of viscoelastic properties between the neat polymers, the effect of testing temperature on the molten state

of each ratio resulting in a wrong comparison of various material flowing state for the same material or even for neat PLA, are indeed expected. Then, to determine phase separation from viscoelastic characteristics of each of the PLA/PBS blending ratio, which included complex viscosity ($\eta^*(\omega)$), dynamic viscosity ($\eta'(\omega)$), loss viscosity ($\eta''(\omega)$), normalization method for each testing temperature was needed prior to apply temperature superposition concept. By doing so, the data of $\eta'(\omega)$ and $\eta''(\omega)$ for each blending ratio were divided with $\eta_{ref}^*(\omega)$ from the individual testing temperature to obtain the data at a similar material flowing characteristic of each blending ratio for the four testing temperatures. Next, the temperature invariant characteristic of the linear viscoelastic properties or a plot of $\eta''(\omega)/\eta_{ref}^*(\omega)$ and $\eta'(\omega)/\eta_{ref}^*(\omega)$ was used to determine for the maximum blending ratio.

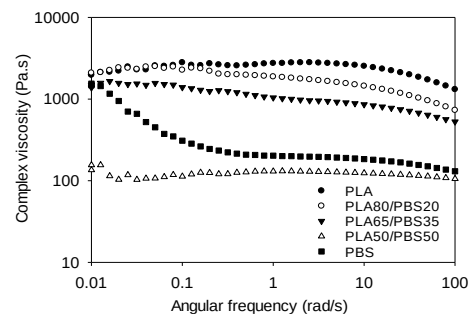


Figure 8. Complex viscosity versus frequency at 170°C of neat PLA, PBS and PLA/PBS blends

The complex viscosities of neat PLA, PBS and all blending ratios of PLA/PBS as a function of frequency and a constant temperature exhibited shear thinning behavior, for instant, data profiles at 170°C shown in Figure 8. The complex viscosity of the blend can be decreased by adding PBS, however, lowering the complex viscosity was limited due to immiscible phase. On the other hand, testing sample of PBS content beyond 35% by mass showed unacceptable miscible level or phase separation. Bhatia *et al.* (2007) suggested that the blending ratios of PLA/PBS that their complex viscosities were fallen between the levels for neat PLA and PBS, samples appeared as a single phase. Even so, the results of their research showed that PLA(4032D)/PBS blends up to 20 wt% of PBS content blends showed miscibility. The phase separation may also be in correspondent with a heavy deviation from log-additive rule of a plot between $\log \eta_{ref}^*(\omega)$ and %PBS (Figure 9). From the theoretical point of view, deviation from log-

additive rule usually indicates incompatibility between two or more polymer matrix with similar chemical structure (Utracki, 1983), however precise identification of maximum blending ratio by using log-additive rule alone may be difficult to justify.

In contrast to using one value of $\log \eta_{ref}^*(\omega)$ and %PBS from log-additive rule plot, the phase separation can be better determined from a modified Cole-Cole plot showing temperature invariant of the dependency of η''/η_{ref}^* on η'/η_{ref}^* among various melting temperature for each blending ratio. Figures 10, 11, 12, 13, and 14 illustrated the modified Cole-Cole plot of neat PLA, PBS, PLA80/PBS20, PLA65/PBS35 and PLA50/PBS50, respectively. The concept of temperature superimposed of the modified Cole-Cole plot for determination of phase separation was similar to the one used by Shumsky *et al.* (2010), but a totally different concept of how the normalization value of the complex viscosity was obtained. For neat PLA, modified Cole-Cole plots at 160°C and 170°C were not superimposed with the temperature of 180°C and 190°C due to the fact that at 160°C and 170°C, the heat flow rate was not enough for completely melting the microstructure of PLA. It must be noted here again that the proposed modified Cole-Cole plot as mentioned earlier was already eliminated the effect of temperature on different material flowing state. To validate the proposed concept, the temperature superposition of the four testing temperatures of neat PBS, as shown in Figure 11, was obvious since the heat flow rate at all testing temperatures was more than enough to melt microstructure of PBS (melting temperature of about 115°C). Therefore, any deviation from the temperature superposition concept of the modified Cole-Cole plot of each polymer blend ratio for various testing temperature was an indication of phase separation.

For all blending ratios of PLA/PBS, the Cole-Cole plot of each testing temperature displayed a double circular arc (profiles not shown here), so an incomplete miscible phase was implied. However, an acceptable level of miscible or a single phase was able to obtain from some mixing ratio and indeed the maximum blending ratio was able to draw based on the modified Cole-Cole plot. By taking the concept of temperature invariant characteristic of viscoelastic properties, the profiles of the modified Cole-Cole plot suggested that the homogeneous phase of the PLA/PBS was obtained if the %PBS did not exceed 20%. This result is consistent with research by Deng and Thomas (2015). Deng and Thomas studied the phase morphology by using AFM, optical microscopy and SEM techniques. The ratio of PLA/PBS at 80/20 was found to be homogeneous.

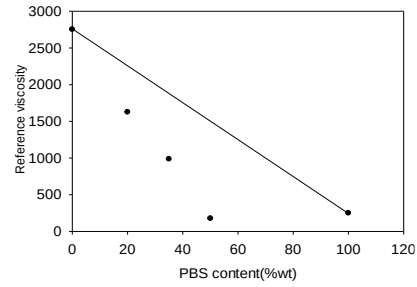


Figure 9. Log-additive rule plots between reference viscosity and %PBS content at 170°C

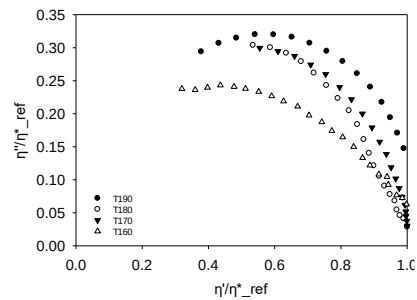


Figure 10. The modified Cole-Cole plot for blend of neat PLA

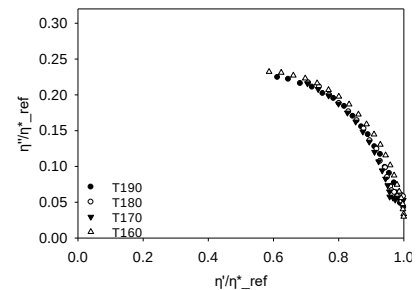


Figure 11. The modified Cole-Cole plot for blend of neat PBS

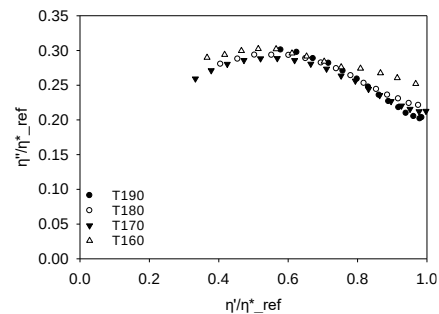


Figure 12. The modified Cole-Cole plot of PLA80/PBS20 blend

Modeling of Flow Behavior for PLA/PBS Blends

One of the main purposes of this study is to obtain the rheological model for viscosity prediction of PLA/PBS blends as a function of shear rate, temperature and PBS content. Steady shear rate testing to characterize the melt flow behavior was conducted at four temperatures (160°C, 170°C, 180°C, and 190°C) and each melting temperature was scanned from the shear rate of 0-1,000 s⁻¹. Rheological testing results of the melting compounds were numerically analyzed based on a nonlinear regression method and found that the shear viscosities of all compounds were fitted well with the Cross model (Equation 2).

$$\eta = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{(1 + (k\dot{\gamma})^m)} \right] \quad (2)$$

where η_0 is zero shear (Pa.s), η_{∞} is infinite shear (Pa.s), k is a constant with time dimension (s) and m is dimensionless parameter. In this study, four unknown parameters were optimized simultaneously from the apparent shear viscosities of shear rate between 0.001-10 s⁻¹ by using a nonlinear regression method. It should be noted here that the η_0 , η_{∞} , k and m were implicit functions of temperature and %PBS content and each function was obtained by a surface response analysis. Relations of η_0 , η_{∞} , k , and m were shown in Equations (3) to (6) and their unknown coefficients were summarized in Table 2.

$$\eta_0 = a_0 e^{-0.5 \left[\left(\frac{T-x_0}{b_0} \right)^2 + \left(\frac{PBS-y_0}{c_0} \right)^2 \right]} \quad (3)$$

$$\eta_{\infty} = y_1 + a_1 T + b_1 PBS + c_1 T^2 + d_1 PBS^2 \quad (4)$$

$$k = a_2 e^{-0.5 \left[\left(\frac{T-x_2}{b_2} \right)^2 + \left(\frac{PBS-y_2}{c_2} \right)^2 \right]} \quad (5)$$

$$m = y_3 + a_3 T + b_3 PBS + c_3 T^2 + d_3 PBS^2 \quad (6)$$

where T is temperature (°C), PBS is mass fraction of PBS ($0 \leq PBS \leq 1$) and a_0 , x_0 , y_0 , b_0 , c_0 , y_1 , a_1 , b_1 , c_1 , d_1 , a_2 , x_2 , y_2 , b_2 , c_2 , y_3 , a_3 , b_3 , c_3 , d_3 are coefficients for Equations (3) to (6).

The predictive model of melt viscosity, Cross model, for each blending compound and melting temperature contained its own set of zero shear and infinite shear viscosities. Since the zero-shear viscosity can predict yield stress intensity, which has implications for the energy required at the beginning of flow and the infinite shear viscosity values can predict the maximum shear thinning of

PLA/PBS blends, different set of their values for all compounding ratios implied that PBS had profound effect on altering the melt viscosity.

Validation of shear viscosity model for the influence of temperature on blends (PLA65/PBS35 at 170°C and 180°C), and influence of PBS content on blends (180°C at PLA80/PBS20 and PLA65/

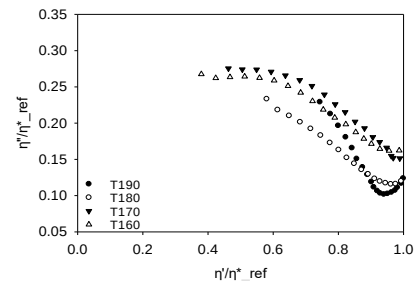


Figure 13. The modified Cole-Cole plot of PLA65/PBS35 blend

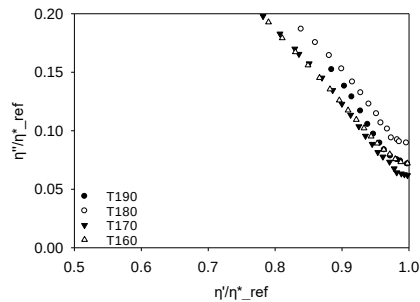


Figure 14. The modified Cole-Cole plot of PLA50/PBS50 blend

Table 2. Parameters for the Equations (3) to (6)

Model parameter ¹	Value
a_0	19 91.060
x_0	164.097
y_0	0.254
b_0	-11.487
c_0	0.115
y_1	-3613.979
a_1	45.427
b_1	292.952
c_1	-0.132
d_1	-1725.225
a_2	16554000277.675
x_2	-273.665
y_2	2.309
b_2	113.361
c_2	-0.381
y_3	-15.768
a_3	0.173
b_3	7.964
c_3	0.000
d_3	-12.855

¹The parameter can be used for shear rate between 0.001-10 s⁻¹

PBS35) were proved for the predictive suitability as displayed in Figures 15 and 16, respectively. The result of validation for the influence of temperature on blends showed that the predictive curves can fit well to the experimental data (Figure 15) and R^2 of these results are 0.943 and 0.929 for PLA65/PBS35 at 170°C and 180°C, respectively. In addition, the result of validation for influence of PBS content on the blends showed that the predictive curve can fit well to the experimental data too (Figure 16) and R^2 of these results are 0.833 and 0.900 for PLA80/PBS20 and PLA65/PBS35, respectively. From the results of validation, the proposed model developed in this research can be used effectively as a tool in prediction of the shear viscosity of PLA/PBS blends as a function of both the temperature and PBS content. Although, the proposed model can predict the flow behavior of PLA /PBS blends, the limitation of the model was in the temperature range of 160°C-180°C and shear rate of 0.001-10 s^{-1} . In addition, the model cannot directly indicate for phase separation of blends. Even so, the model can provide a guideline for adjustment of process parameters from shear viscosity of the PLA/PBS.

Conclusions

The principle of temperature invariant of the viscoelastic properties of the polymer blend was employed in studying the compatibility of the PLA/PBS blends. Modification form of Cole-Cole plot was proposed to eliminate the effect of testing temperature on the flowing state of the melt allowing us to apply the principle of temperature invariant for determination of the phase separation. With this technique, the rheological parameters were extremely sensitive to differentiate the transition from a homogeneous phase to a heterogeneous phase as a result of both mixing ratio and melting temperature. The rheological behavior in term of shear viscosity for PLA/PBS blend exhibited shear thinning behavior and the influences of %PBS and melting temperature on the shear viscosity were predicted by Cross model. Predictive results were found to be in good agreement with measuring data within the shear rate range of 0.001-10 s^{-1} .

Acknowledgement

This work was financially supported by the National Innovation Agency (Thailand) and National Research Council of Thailand. The authors would like to thank Suranaree University of Technology for experimental location and partially equipment support.

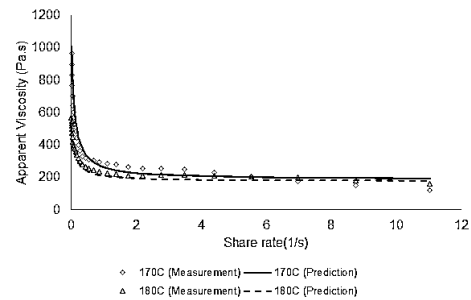


Figure 15. Apparent viscosity of PLA/PBS blends (65/35) at 170°C and 180°C

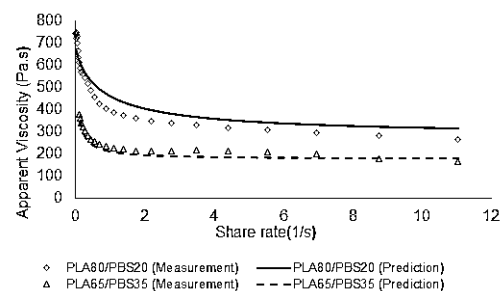


Figure 16. Apparent viscosity of PLA/PBS blends (80/20, 65/35) at 180°C

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