

Rheological and mechanical properties of poly(lactic acid)/polystyrene polymer blend

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Abstract Properties modification by blending polymers has been an area of immense interest. In this work, rheological and mechanical properties of poly(lactic acid)/polystyrene (PLA/PS) blends were investigated. PLA/PS blends in different ratios were prepared using a laboratory scale single screw extruder to obtain (3 mm) granules. Rheological properties were studied using a capillary rheometer and the Bagley's correction was performed. True shear rate ($\dot{\gamma}_r$), true shear stress (τ_r), and true viscosity (η_r) were determined, the relationship between true viscosity and ($1/T$) was studied for PLA70 blend and the flow activation energy at a constant shear stress (E_τ) and a constant shear rate ($E_{\dot{\gamma}}$) was determined. The mechanical property measurements were performed at room temperature. Stress at break and strain at break were determined. The results showed that PLA/PS blend exhibited a typical shear-thinning behavior over the range of the studied shear rates, and the viscosity of the blend decreased with increasing PLA content. Also it was found that no equal-viscosity temperature exists between PLA and PS. The mechanical results showed immiscibility between PLA and PS in the blend.

Keywords PLA · PS · Polymer blends · Rheology · Mechanical properties

Introduction

Biodegradable polymers have been around for almost a decade, but it has only been in the last 9–10 years that they have started to be produced on a commercial scale. Biodegradable polymers have already found acceptance in application areas such as

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food packaging, bags, and sacks, loose fill packaging agricultural film and many niche market applications. However, while they remain very much a niche product at the moment, there are signs that biodegradable polymers are ready to attack mass markets. This kind of polymer, which is prepared from renewable resources, can be easily synthesized and disposed after use by biodegradation. In the history of biodegradable polymers, polyesters played a dominant part just from the beginning of the development; one of the first products developed as biodegradable polymers from the beginning of the 1970s was poly(lactic acid) (PLA).

Poly(lactic acid) is a compostable polymer derived from renewable sources (mainly starch and sugar). Until the last decade, the main uses of PLA have been limited to biomedical and pharmaceutical applications such as implant devices, tissue scaffolds, and internal sutures, because of its high cost and low molecular weight. Since, the existence of both hydroxyl and a carboxyl group in lactic acid enables it to be converted directly into polyesters via a polycondensation reaction. However, the conventional condensation polymerization of lactic acid does not increase molecular weight sufficiently, so conventional polycondensation of lactic acid yields a brittle glassy polymer, which is unusable for most applications.

The most common way to obtain high molecular weight of PLA (greater than 100,000 Da) is through two steps ring-opening polymerization of lactide [1]. In this way, intermediate lactide (cyclic dimer of lactic acid) is formed in the first step, and after removing condensation product water, the PLA oligomer is depolymerized to lactide; in the second step, purified lactide converted into corresponding high-molecular weight polyesters by catalytic ring-opening polymerization. These new techniques in synthesizing PLA, which allow economical production of high molecular weight PLA polymer, have broadened its uses.

High molecular weight PLA can be processed into fibers, and articles with rigidity and strength, which are useful at commodity scale, it has reasonably good optical, physical, mechanical, and barrier properties compared to existing petroleum-based polymers for example, the permeability coefficients of CO₂, O₂, N₂, and H₂O for PLA are lower than for polystyrene (PS), but higher than poly(ethylene terephthalate) (PET). Oriented PLA provides better performance than oriented PS, but comparable to PET. Overall, PLA has the required properties desirable for a number of applications to compete with existing petroleum-based plastics. However, some of other properties such as, low melt viscosity, impact strength, and heat distortion temperature are frequently inadequate for various end-user applications.

Properties of PLA can be modified by polymer blending techniques, where it was blended with several synthetic and biopolymers in efforts to enhance its properties and also to obtain novel materials. PLA have been blended with rubbers [2], thermoplastic starch (TPS) [3–8], poly(butylene succinate) (PBS) [9], poly(butylene succinate adipate) (PBSA) [10], poly(butylene adipate-co-terephthalate) (PBAT) [11–14], acrilonryl-butadiene-styrene (ABS) [15], polypropylene (PP) [16, 17], and polyethylene (PE) [18], to obtain materials with lower cost and improved properties.

PS is one of the cheapest synthetic polymers and it has a lot of applications. However, PS has poor degradability and is high hydrophobic. This makes it difficult

to dispose the PS articles after use. Therefore, PS was blended with TPS which was prepared by using different plasticizers (glycerol, buriti oil) [19–22], in efforts to enhance the degradability of PS, and it was found that PS's degradability can be improved when TPS is added to it. So, blending of PLA with PS might be a good way to balance the cost effective issue and enhance the degradability of PS.

In this article, poly(lactic acid), polystyrene blends were prepared in different ratios using a single screw extruder (SSE), and the aim of this work is to study the rheological and mechanical properties of PLA/PS polymer blends. Such works are very important in the development of composites and blends from biodegradable polyesters.

Experimental

Materials

Poly(lactic acid) (PLA) (ESUNTM A-1001) [density = 1.25 g/cm³ (21.5 °C), MFI = 12.5 g/10 min (190 °C/2.18 kg)] was supplied by Bright China Industrial Company. Ltd (Shenzhen, China), the selected grade is an extrusion material; it was dried at 70 °C for 6 h before using. Polystyrene (PS) (SABIC[®] 125PS) [density = 1.05 g/cm³, MFI = 7 g/10 min (200 °C/5 kg)] was supplied by Sabic (KSA).

Blends preparation

Blends of PLA/PS in different ratios were prepared using a laboratory scale single screw extruder (SSE) ($D = 20$ mm, $L/D = 25$) [SHAM EXTRUDER 25D Performance: *Kreem Industrial Establishment*, Damascus—Syria], it could be operated at different speeds, varied from 0 to 100 rpm. The screw has a fluted type mixing section located before the metering zone [23], in this type of mixers the material is forced to pass at a high shear stress. This brings in some level of dispersing action besides reorienting the interfacial area, and increasing the imposed total strain. The flight depth of screw in the metering zone was 1.5 mm, and the helix angle 17.7°. PT124G-124 melt pressure transducer (Shanghai Zhaohui Pressure Apparatus Co., Ltd, China) was located in the die head for measuring the melt pressure.

The screw speed was set at 20 rpm in the blends preparation, and the extruder temperature profile along the barrel was 130, 140, 150, 160 °C (from feed zone to die). The blends were extruded through a multi holes die (3 mm), the extrudates were then fed into a granulator, which converted them into granules. The obtained granules were dried at 70 °C for 6 h before studying. The prepared blends and the pure polymers were then compression molded (12 MPa) for 5 min and the molding temperature for PLA, PS, and their blends were 150, 180, and 150 °C, respectively. Molded specimens were then cooled to 80 °C before removal from the mold and cut into a dog bone-shaped sample (ASTM D638) under the air pressure for mechanical testing. All samples and granules were kept in plastics bags prior to using. The compositions of the blends are shown in Table 1.

Table 1 Compositions of PLA/PS blends

Sample	PLA100	PLA70	PLA50	PLA30	PLA0
PLA (wt%)	100	70	50	30	0
PS (wt%)	0	30	50	70	100

Rheology

Rheological properties of the blends were studied using a capillary rheometer (Davenport 3/80); it consists of a barrel into which material was loaded before being pushed by a plunger through a capillary; the load in the plunger provides the total pressure drop in the barrel and capillary and the volume flow rate. The rheological experiments were carried out at 165, 175, 185, 195 °C, and by using $L/R = 8, 15, 25, 36$ capillaries. Bagley's correction [24, 25] was performed by using the data from the four capillary dies. The true shear rate ($\dot{\gamma}_r$) is given by:

$$\dot{\gamma}_r = \frac{3n + 1}{4n} \frac{4Q}{\pi R^3} \quad (1)$$

where R is the capillary radius, n is the non-Newtonian index depending on temperature, and Q is the volumetric flow rate. The term $\left(\frac{3n+1}{4n}\right)$ was the Rabinowitsch correction factor [24].

The true shear stress (τ_r) is given by:

$$\tau_r = \frac{\Delta P}{2\left(\frac{L}{R} + e\right)} \quad (2)$$

where ΔP is the pressure at the capillary entrance, L is the capillary length, and e is the Bagley's correction factor.

True viscosity is given by:

$$\eta_r = \frac{\tau_r}{\dot{\gamma}_r} \quad (3)$$

The values of flow activation energy at a constant shear stress (E_τ) and a constant shear rate ($E_\dot{\gamma}$) were determined by using Arrhenius equation:

$$\eta_r = A e^{\frac{E}{RT}} \quad (4)$$

where A is the consistency related to structure and formulation, R is the gas constant (8.314 J/mol K).

Mechanical properties

Tensile testing to study stress at break (N/mm^2) and strain at break (%) were performed by using Testometric M350-10KN (The Testometric Company Ltd, Rochdale, UK) at room temperature, all samples were strained at 5 mm/min. Samples were conditioned at room temperature for a period of 48 h prior to testing. Results from 3 to 5 specimens were averaged.

Results and discussion

Rheological properties

Flow curves

For evaluating the processing behavior, the flow curves of these blends were determined. Figure 1 shows the flow curves of all sample melts at 165 °C and $L/R = 15$.

It can be noted from Fig. 1 that the linearity of these lines is excellent and they obey the power law in a certain range of shear rate:

$$\tau = K\dot{\gamma}^n \quad (5)$$

The non-Newtonian index n was calculated from the slope of the fitted lines, the value of n exhibits substantially the sensitivity of viscosity to the shear rate. All the values of n were less than 1, implying that PLA/PS blend melts were pseudo plastic; similar to most of the polymeric melts.

Viscosity curves

The true viscosity of the PLA/PS blends as a function of the true shear rate is shown in Fig. 2, at 165 °C and $L/R = 15$. PLA, PS, and their blends show a typical shear-thinning behavior over the range of the studied shear rates, this behavior was attributed to the alignment or arrangement of chain segments of polymers in the direction of applied shear stress [26]. Figure 3 shows the relationship between true viscosity and PLA content in the blend. It can be clearly seen from Fig. 3, that the viscosity of PS is higher compared to that of pure PLA and the viscosity of the blend increases with increasing PS content in the blend, this effect becomes more and more pronounced as PS content increases. This phenomenon is due to PS high

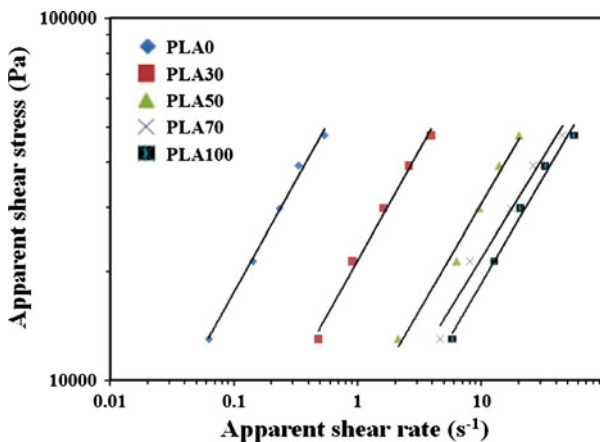


Fig. 1 Flow curves of PLA/PS blends (165 °C, $L/R = 15$)

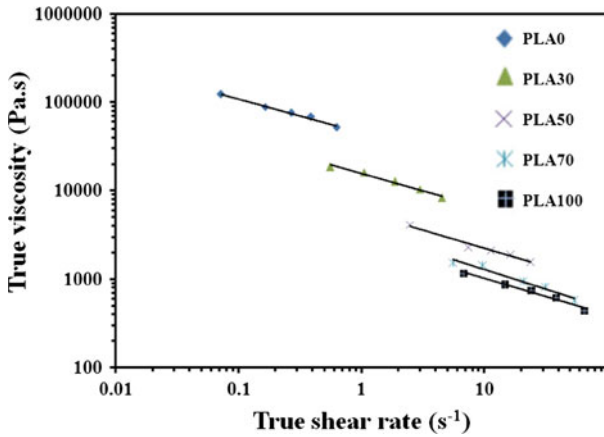


Fig. 2 True viscosity versus true shear rate of the blends (165 °C, $L/R = 15$)

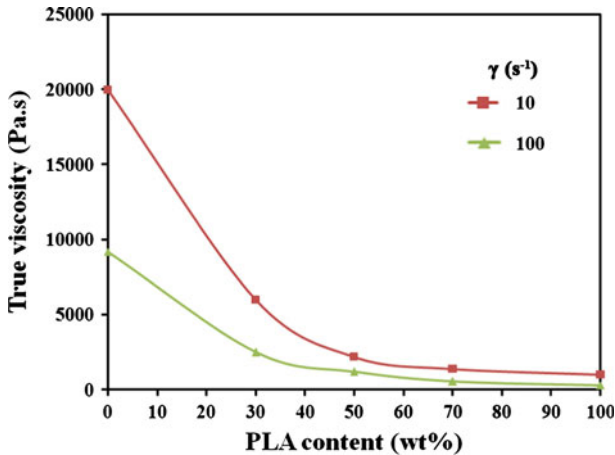


Fig. 3 True viscosity versus PLA content (wt%) (165 °C, $L/R = 15$)

viscosity. These results are important since they indicate that the optimal processing conditions for shaping operations of PLA/PS blends could be quite different as compared to those for pure PLA. Adding 30% PLA to PS dropped the true viscosity (at $\gamma = 10 \text{ s}^{-1}$) by a factor of 0.7 which is outside of the mixing rule as shown in Fig. 3, this result might indicate to poor compatibility or incompatibility between PLA and PS.

Flow activation energy

The plots of true viscosity versus $1/T$ for PLA70 ($L/R = 15$) at a constant shear stress (E_τ) and a constant shear rate (E_γ) are shown in Figs. 4 and 5, respectively.

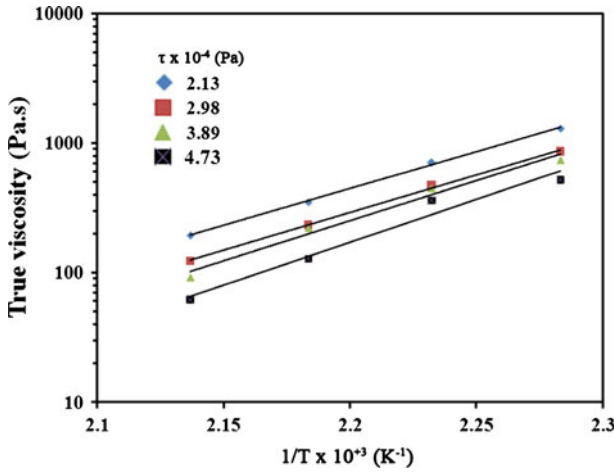


Fig. 4 True viscosity versus $1/T$ of PLA70 at a constant shear stress ($L/R = 15$)

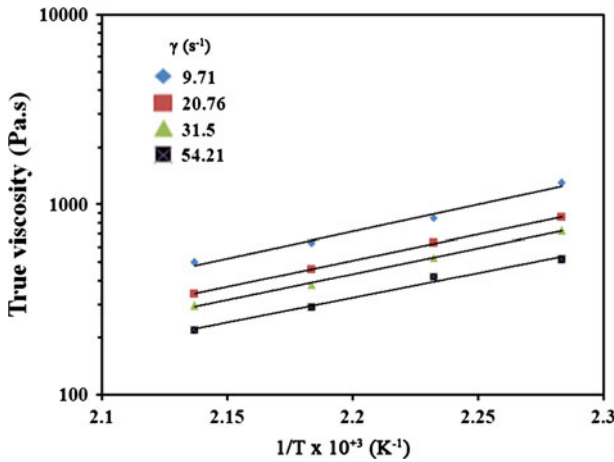


Fig. 5 True viscosity versus $1/T$ of PLA70 at a constant shear rate ($L/R = 15$)

Good linearity for all curves was observed. E_τ and E_γ could be obtained from the slope of these lines:

$$E_\tau = R \left(\frac{d \log \eta_r}{d(1/T)} \right)_\tau \tag{6}$$

$$E_\gamma = R \left(\frac{d \log \eta_r}{d(1/T)} \right)_\gamma \tag{7}$$

The values of E_τ and E_γ for PLA70 are listed in Table 2. The melt viscosity of polymer was relative to the structure and free volume. The increase in temperature

Table 2 The values of flow activation energy for PLA70 blend at a constant shear stress and a constant shear rate

$\tau \times 10^{-4}$ (Pa)	2.13	2.98	3.89	4.73
E_τ (KJ/mol)	108.9	111.4	119.8	126.04
$\dot{\gamma}$ (s^{-1})	9.71	20.76	31.5	54.21
$E_\dot{\gamma}$ (KJ/mol)	54.04	52.71	51.96	50.21

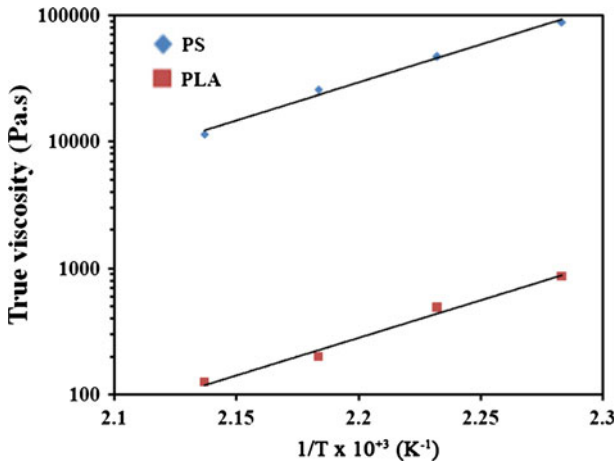


Fig. 6 True viscosity versus $1/T$ of PLA and PS at $\tau = 2.13 \times 10^4$ Pa ($L/R = 15$)

might result in the enhancement of free volume and improvement of chains mobility and thus lead to weakening the melt viscosity, so the viscosity decreased exponentially with the temperature rising. It is well known that the value of flow activation energy reflects the temperature-sensitivity of viscosity, so the more E_τ or $E_\dot{\gamma}$ was the more sensitive the behavior of blends were to the temperature. It could be noted from the values of E_τ and $E_\dot{\gamma}$ that E_τ increases with increasing shear stress, while $E_\dot{\gamma}$ decreases with increasing shear rate. Also, it could be noted that $E_\tau > E_\dot{\gamma}$ ($\frac{E_\dot{\gamma}}{E_\tau} < 1$) which confirms that PLA70 is a pseudo plastic material [27].

Figure 6 shows the relationship between true viscosity and $1/T$ for PLA and PS at $\tau = 2.13 \times 10^4$ Pa, it could be observed that the lines in Fig. 6 are parallel, which implies that no equal-viscosity temperature (T^*) (the temperature at which PLA and PS have the same viscosity), exists between PS and PLA at this shear stress, the same behavior was noted in PS/PMMA blend [24]. The advantage of the existence of an equal-viscosity temperature for blend constituents is obvious. If mixing is performed at around T^* , high compounding efficiency would be expected because the viscosities of the two components are close. Besides, it is favourable for controlling the morphology of the blend.

Mechanical properties

For all samples PLA, PS, and their blends, no yield phenomenon is existed. The stress at break of the blends versus PLA content is shown in Fig. 7.

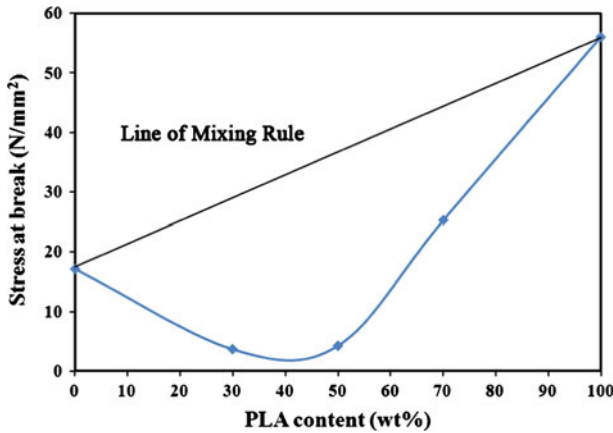


Fig. 7 Stress at break versus PLA content (wt%)

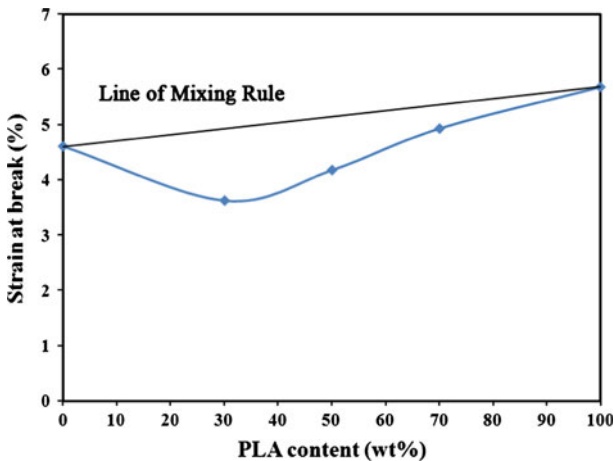


Fig. 8 Strain at break versus PLA content (wt%)

The stress at break of blends decreased at up to 40 wt% PLA contents and slightly increased at more than 40 wt% PLA contents. This kind of results that the stress at break values are below the line of the mixing rule, could be seen in typical immiscible polymer blends, so it was to say that PLA and PS are immiscible as the stress at break values were far below the line of mixing rule (negative deviation) [28]. The strain at break as a function of PLA contents is shown in Fig. 8, the strain at break shows nearly a similar behavior to stress at break, where the strain at break of blends decreased at up to 30 wt% PLA contents, and increased at more than 30 wt%.

Various degrees of compatibility (old term of miscibility) are possible in polymer blends ranging from complete miscibility to phase separation. Compatibility is a function of the interaction of polymer molecules in the blend and can be detected

by using various methods including mechanical and interfacial measurements. The mechanical properties of blends vary between those of the pure polymers comprising the blend. In the compatible blends, the mechanical properties show a linear relationship (Line of mixing rule) between blend composition and such mechanical properties as stress at break and strain at break. In general, a negative deviation from the linear relationship is considered an indication of immiscibility or poor compatibility between blend components, whereas a positive deviation is considered an indication of improved compatibility. So it was to say that PLA and PS form an incompatible polymer blend system.

Biresaw and Carriere [29] have studied the compatibility of PS/biodegradable polyesters blends, where the tensile properties of blends of PS with each of PLA, polycaprolactone (PCL) and Eastar Bio Ultra[®] (EBU) were investigated. They found that the compatibility between PS and PCL is better than that between PS and EBU, whereas the compatibility between PLA and PS was not evaluated because only the 25% PS blend was molded and studied, so more data were needed to evaluate the compatibility between PLA and PS.

Conclusion

The rheological and mechanical properties of poly(lactic acid)/polystyrene (PLA/PS) blends were studied. The blends were prepared using a single screw extruder (SSE). As can be concluded from the above discussion, PLA/PS blend is shear-thinning. The viscosity of the blend decreases with increasing PLA content which was attributed to PS high viscosity. The flow activation energy at a constant shear stress of PLA70 increases with increasing shear stress, but at a constant shear rate the flow activation energy decreases with increasing shear rate. No equal-viscosity temperature (T^*) exists between PS and PLA at $\tau = 2.13 \times 10^4$ Pa. The mechanical results shown here strongly support the notion that PLA/PS is an incompatible blend. The relative high viscosity (compared to pure PLA) and the fully biodegradability of PLA, make PLA70 suitable to produce low cost and semi-biodegradable material with enhanced processability.

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