

Melt Rheology of Poly(Lactic Acid)/Low Density Polyethylene Polymer Blends

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Abstract

In this work, rheological properties of poly(lactic acid) (PLA), low density polyethylene (LDPE) polymer blends were investigated in the molten state. The experiments were carried on a capillary rheometer. The effect of shear stress, temperature and blending ratio on the flow activation energy at a constant shear stress and melt viscosity of the blends are described. The results showed that the PLA/LDPE polymer blends are pseudo plastic in nature, where their viscosity decreases with increasing shear stress. Also it was found the melt viscosity of the blends decreases with increasing PLA content in the blend.

Keywords: PLA, LDPE, Polymer Blends, Melt Viscosity, Flow Activation Energy

1. Introduction

Two or more existing polymers may be blended for various reasons. One reason is to achieve a material that has a combination of the properties of the constituents, e.g. a blend of two polymers, one of which is chemically resistant and the other tough. Another reason is to save costs by blending a high-performance polymer with a cheaper material. Blending also benefits the manufacturer by offering: 1) Improved processability, product uniformity, and scrap reduction. 2) Quick formulation changes. 3) Plant flexibility and high productivity. 4) Reduction of the number of grades that need to be manufactured and stored. 5) Inherent recyclability, etc [1].

Poly(lactic acid) (PLA) is well known aliphatic polyesters derived from corn and sugar beets, and degrades into nontoxic compounds in landfill. It can be synthesized from direct condensation of lactic acid or by ring-opening polymerization of cyclic lactide [2], 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. PLA was chosen for its high biocompatibility and biodegradability. It has become an alternative to traditional commodity plastics for everyday applications as an environmental friendly polymer due to its some unique properties such as high strength, high stiffness and resistance to fats and oil. However, brittleness and other properties such as low viscosity, low thermal stability, high moisture sensitivity, medium gas barrier properties, high cost (comparing with PE, PP, PS...) and low solvents resistance (e.g., against water) of the pure polymer are often insufficient for a lot of 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 [3], thermoplastic starch (TPS) [4-9], poly(butylene succinate) (PBS) [10], poly(butylene succinate adipate) (PBSA) [11], poly(butylene adipate-co-terephthalate) (PBAT) [12-15], acrylonitril-butadiene-styrene (ABS) [16], polypropylene (PP) [17-19], and polystyrene (PS) [20,21], to obtain materials with lower cost and improved properties.

Polyolefin's industry is still a very dynamic business, where low density polyethylene (LDPE) plays a key role and it has a wide range of applications. LDPE has good properties such as, low cost, processability, resilience and moisture insensitivity. However, the use of LDPE causes serious environmental concerns because it is not

biodegradable; *i.e.*, it is not biodegraded by the microorganisms present in the environment. Even though recycling has become an alternative, not all post-consumer products may be recycled and, in some cases, this process is not economically sustainable. The waste management problem has prompted the development of, at least, partially degradable plastics, a fact that may be achieved by blending with biodegradable fillers, which can effectively reduce the volume of plastic waste by partial degradation. Therefore, LDPE was blended with native starch or thermoplastic starch (TPS) in efforts to enhance its degradability [22], and it was found that LDPE's degradability can be improved when starch is added to it, although the pure LDPE is not biodegradable. However, the addition of TPS might negatively affect the properties of LDPE. In this case PLA, which has good mechanical properties, can be used as alternative to TPS. Studies on PLA/PE blends were reported by many authors [23-25].

Blends PLA with LDPE offer cost-performance benefits, and enhance the degradability of LDPE. In this work PLA/LDPE blends were prepared using a laboratory scale single screw extruder and characterized in terms of the rheological properties. Such works are very important in the development of composites and blends from biodegradable polyesters. No attention has been given in the past to rheological characterization of PLA/LDPE polymer blends.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) (ESUN™ 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. Low density polyethylene (LDPE) (SABIC®LDPE2308TN00) [density = 0.924 g/cm³, *MFI* = 7.5 g/10 min (190°C/2.16 Kg)] was supplied by Sabic (KSA).

2.2. Blends Compounding

Blends of PLA/LDPE in different ratios were compounded 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 device located before the metering zone [26], which can extend the compounding ability of the SSE, 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 Zhao-hui Pressure Apparatus Co., Ltd-China) was located in the die head for measuring the melt pressure.

The screw speed was set at 70 rpm in the blends preparation, and the extruder temperature profile along the barrel was 180°C, 190°C, 200°C, 210°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 compositions of the blends are shown in **Table 1**.

2.3. Rheology

Rheological properties of the blends were studied using a constant pressure circular capillary rheometer. The melt is extruded by the use of dead weights (*i.e.* constant pressure) rather than constant plunger speed. This instrument, popularly known as the Melt Flow Indexer (MFI), is very popular in the thermoplastics industry due to its ease of operation and low cost, which more than compensates for its lack of sophistication. The parameter measured through the melt flow indexer contains mixed information of the elastic and viscous effects of the polymer. The rheological experiments were carried out at 175°C, 180°C, 185°C and 190°C, and by using *L/R* = 8, 15, 25 and 36 capillaries. Bagley's correction [27,28] was performed by using the data from the four capillary dies. The apparent shear rate (γ_a) is given by:

$$\gamma_a = \frac{4Q}{\pi R^3} \quad (1)$$

where *R* is the capillary radius, and *Q* is the volumetric flow rate. The true shear rate (γ_r) is given by:

$$\gamma_r = \left(\frac{3n+1}{4n} \right) \gamma_a \quad (2)$$

where *n* is the non-Newtonian index depending on temperature, the term $((3n+1)/4n)$ was the Rabinowitsch correction factor. The apparent shear stress (τ_a) is given by:

$$\tau_a = \frac{RP}{2L} \quad (3)$$

Table 1. Compositions of PLA/LDPE blends.

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

where P is the pressure at the capillary entrance, and L is the capillary length. The true shear stress (τ_r) is given by:

$$\tau_r = \frac{P}{2(L/R + e)} \quad (4)$$

where e is the Bagley's correction factor. The true viscosity (η_r) is given by:

$$\eta_r = \frac{\tau_r}{\dot{\gamma}_r} \quad (5)$$

The values of flow activation energy at a constant shear stress (E_τ) were determined by using Arrhenius equation form:

$$\eta_r = A \cdot e^{\frac{E_\tau}{RT}} \quad (6)$$

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

3. Results and Discussion

3.1. Flow Curves

The flow curves, ie plots of shear stress versus shear rate for PLA/LDPE blends covering the whole composition range have been measured over a temperature range from 175°C to 190°C in steps of 5°C. A typical result for the plot at 175°C is shown in **Figure 1**.

It can be seen that these curves apparently deviate from linear relationship inclining to the axis of shear rate, which means that the homopolymers of PLA, LDPE and their blends are pseudo plastic non-Newton fluids similar to most polymeric melts, and they obey the power law:

$$\tau = K \cdot \dot{\gamma}^n \quad (7)$$

where K is the consistency index and n is the non-Newtonian index, which can be calculated from the slope of

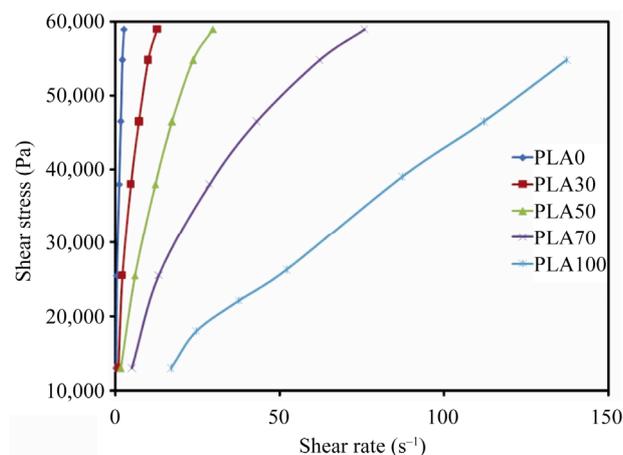


Figure 1. Flow curves of the blends at 175°C.

the lines in **Figure 1**.

$$n = \frac{d \log \tau}{d \log \dot{\gamma}} \quad (8)$$

Figure 2 shows the values of n for PLA/LDPE blend melts over blending ratio at 175°C. It could be noted from **Figure 2**, that the values of n were less than 1, implying that PLA/LDPE blend melts were pseudo plastic; similar to most polymer melts. Also it could be noted from **Figure 2**, that the n values of the blends are less than those of the homopolymers, PLA and LDPE. The value of n describes the deviation from the Newtonian fluids about flow behavior, so it is also called the flow behavior index. A higher value of n reveals less influence of shear rate on flow behavior. In other words, the changes in viscosity upon shear rate are not obvious, so it could be said that the flow behavior of the blend melts is more sensitive to shear rate as compared with the homopolymers.

Also it should be noted from **Figure 2**, that the PLA/LDPE blends found to be incompatible, where they show a drop in n values and PLA50 is the most non-Newtonian ($n = 0.52$). The compatible polymer blends show high non-Newtonian indexes which are closed to that of their major phase (PLA and LDPE).

3.2. Melt Viscosity

Figure 3 shows plots of the melt viscosity versus shear stress for homopolymers PLA, LDPE and the blends at different temperatures. It shows that the viscosity of PLA, LDPE and the blends decreases with increasing shear stress, showing a typical property of pseudo-plastic non-Newton fluids, this behavior was attributed to the alignment or arrangement of chain segments of polymers in the direction of applied shear stress [29].

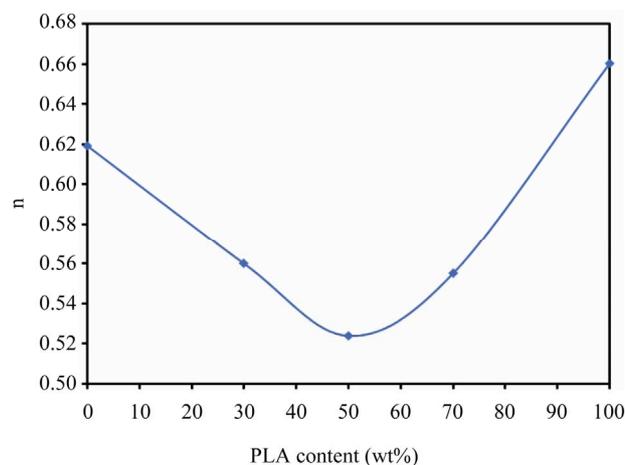


Figure 2. Non-newtonian index of the blends at 175°C.

In order to observe how the melt viscosity varies with the blending ratio at different temperatures, cross plots of **Figure 3** are given in **Figure 4**. The high viscosity at a low shear rate provide the integrity of the extrudate during extrusion, and the low viscosity at a high shear rate

enables low injection pressure, high injection speed and less time of the injection cycle.

It could be noted from **Figure 4** that the melt viscosity of the blend decreases with increasing PLA at 175°C, and this behavior can be attributed to the low melt vis-

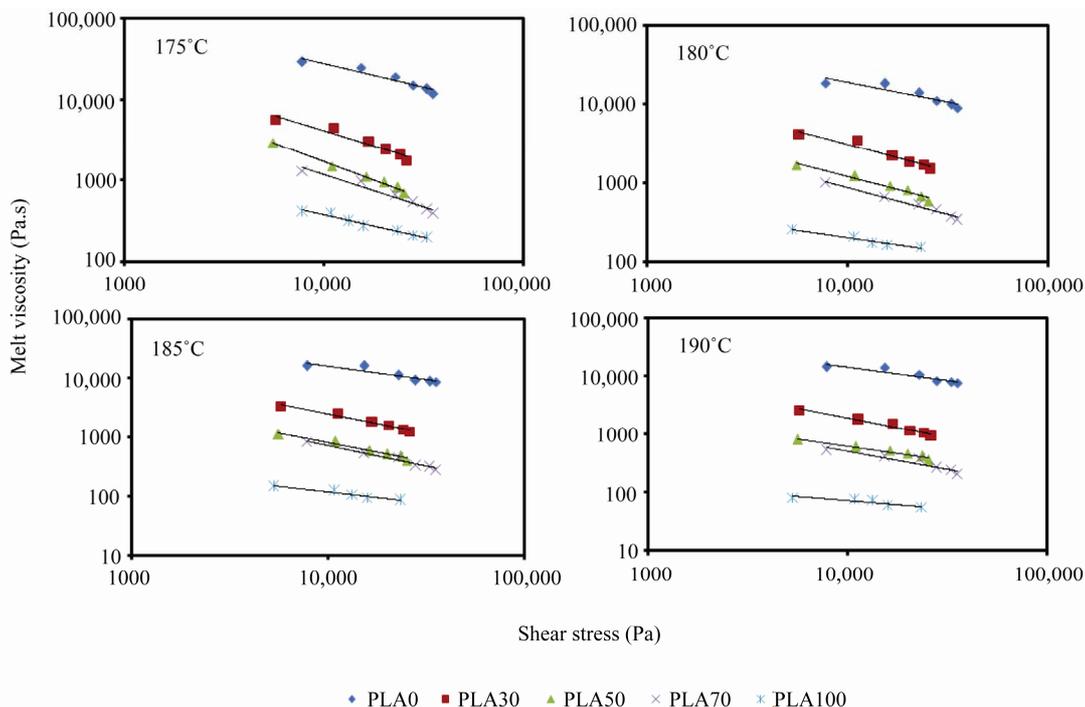


Figure 3. Variation of melt viscosity with shear stress for PLA/LDPE blends.

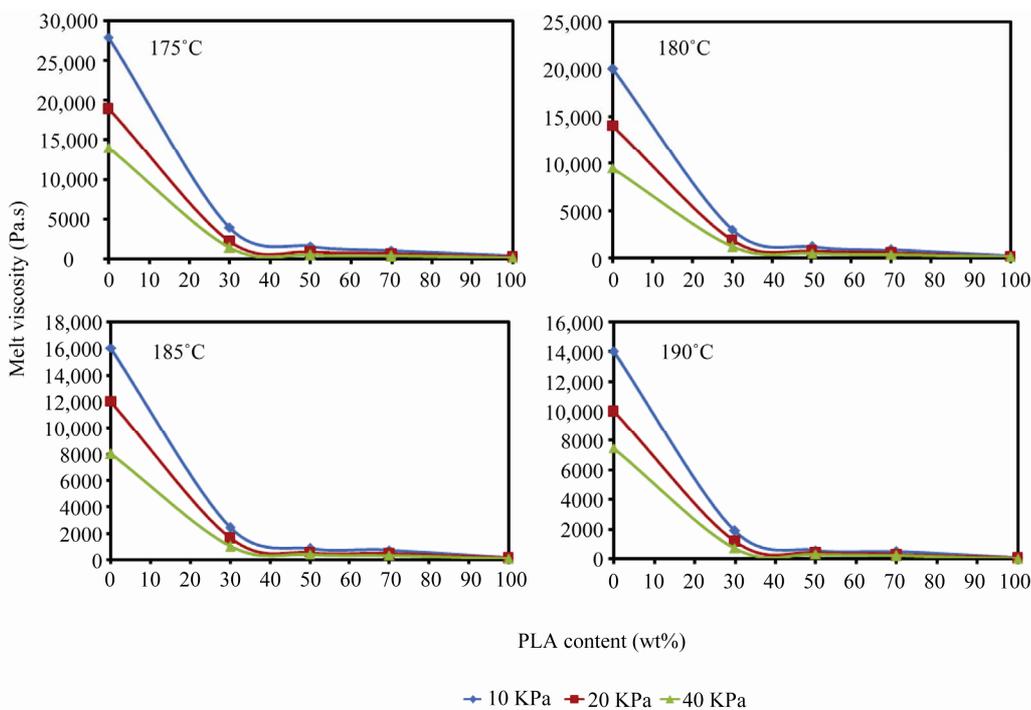


Figure 4. Variation of melt viscosity with blending ratio for PLA/LDPE blends.

cosity of PLA comparing with LDPE. The same behavior can be noted at the different temperatures (180, 185, 190°C). This behavior can be explained according to the flow activation energy of the blends.

The low melt viscosity of the blends makes them suitable to be used in injection molding process. The good processability (low processing temperature or low pressure) of this blend was detected during injection process of the blends by using NEGRI BOSSI (NB 25) injection machine (Lessona Corporation, Italy). **Figure 5** shows samples of the blends and their processing condition (temperature, pressure and cooling time in the mold). It could be noted from **Figure 5** that the injection temperature of the blend decreases with increasing PLA content, which was attributed to the decreasing of the melt viscosity with increasing PLA content in the blend.

3.3. Flow Activation Energy

The true viscosity variation of the blends with temperature at $\tau = 10, 20$ and 40 KPa is shown in **Figures 6**. The true viscosity of PLA, LDPE and all of the blends decreases with increasing temperature. However, the melt

viscosity of PLA changes with temperature much more sharply than that of LDPE. The plots of true viscosity versus $1/T$ shown in **Figures 6**, give a group of straight lines, which indicates that the relationship between the true viscosity and temperature follows Arrhenius equation (Equation (6)). With a rise of temperature the motion ability of polymer chains enhances, and the resistance between the melt layers decreases relevantly, leading to reduction of the melt viscosity. Flow activation energy at a constant shear stress (E_f) could be calculated from the slopes of these lines.

Figure 7 shows the effect of the blending ratio on the flow activation energy, it is clearly seen that the flow activation energy of PLA is greater than that of LDPE, which indicates that the flow behavior of PLA is more sensitive to temperature compared with LDPE. Also, it could be noted from **Figure 7**, that the flow activation energies of PLA/LDPE blends at $\tau = 10^4$ Pa are between those of PLA and LDPE, whereas at $\tau = 4 \times 10^4$ Pa, the flow activation energy of PLA50 is lower than that of LDPE which indicates that the sensitivity of PLA50 viscosity to temperature sharply decreases with increasing shear stress.

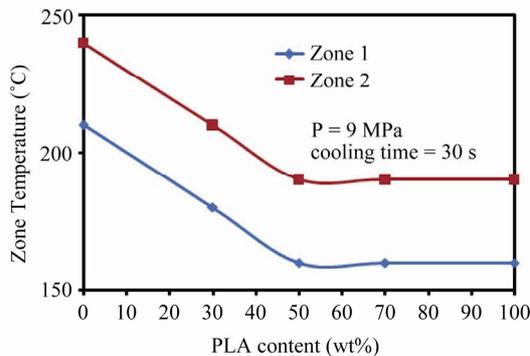


Figure 5. Injected samples and their processing condition.

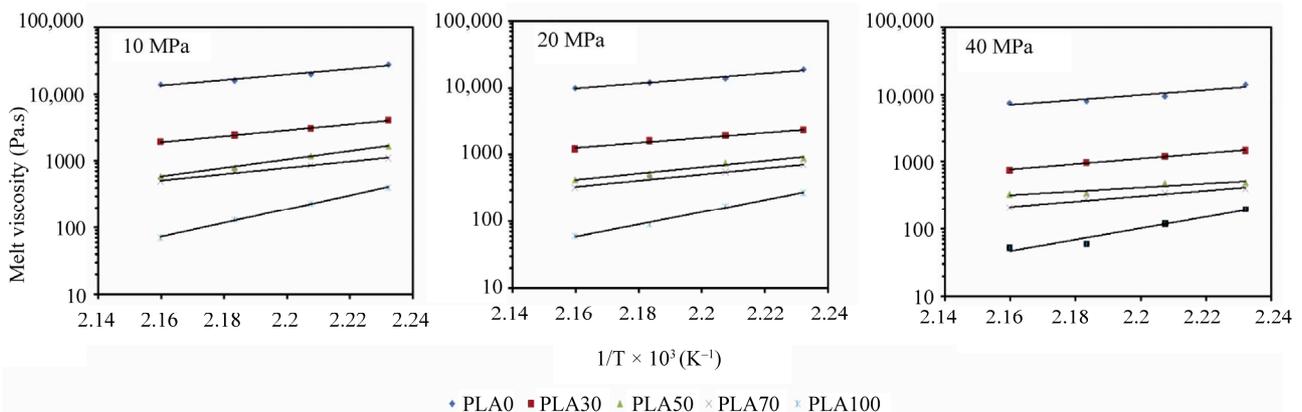


Figure 6. True viscosity versus $1/T$ of the sample melts.

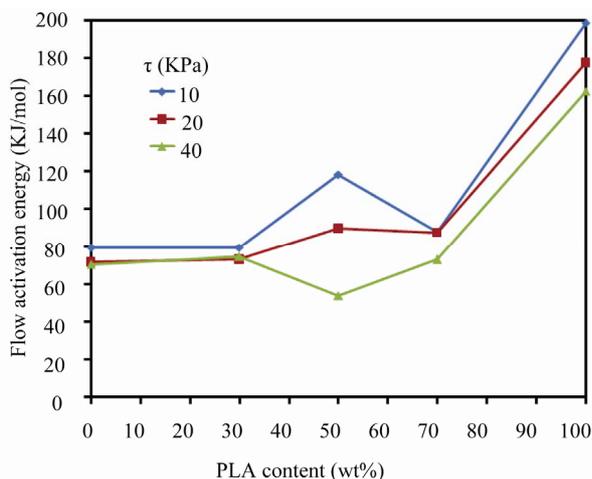


Figure 7. Flow activation energy at a constant shear stress versus PLA content (wt%).

4. Conclusions

In this work, rheological properties of PLA/LDPE polymer blends were studied. The blends were prepared using a single screw extruder. Rheological results showed that PLA/LDPE polymer blends are pseudo plastic in nature; their viscosity decreases with increasing shear rate similar to most polymer melts. The true viscosity of PLA decreases sharply with increasing temperature, whereas the true viscosity of LDPE varies slightly only with temperature. Also it was found that the true viscosity of the blends decreases with increasing PLA content which was attributed to PLA low viscosity. The rheological results indicate that the prepared blends are suitable to be used in injection molding process, where they have low melt viscosity. Such blends are very important in development new biodegradable materials with low cost.

5. References

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