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Abstract The rheological properties and the viscoelastic behaviour of blends of polyethylene with different percentages of poly(lactic acid), ranging from 0 to 100 wt%, were studied. In a first part, all blends were examined under steady conditions using a capillary rheometer (at 180, 190 and 200 °C) and dynamic conditions using a parallel plate rheometer. The results showed that all blends behaved like pseudoplastic fluids, with the power–law index values varying between those of polyethylene and polylactide (0.45–0.75 at 180 °C, 0.49–0.77 at 190 °C and 0.54–0.81 at 200 °C). It was also observed that at low shear rate, pure poly(lactic acid) and polyethylene possessed, respectively, the highest and the lowest flow activation energy (66.9 and 48.3 kJ/mol); however, at high shear rate, the greater the content of poly(lactic acid), the lower the activation energy. In addition, poly(lactic acid) exhibited lower viscosity and lower melt elasticity than either polyethylene or the blends. The dynamic rheological study demonstrated that all formulations displayed shear thinning behaviour and only virgin poly(lactic acid) exhibited a clear Newtonian plateau. Also, mainly at low frequencies, polyethylene had the higher values of storage modulus (325 Pa), loss modulus (937 Pa) and

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complex viscosity (9,740 Pa.s). However, blends had values lying between those of the two homopolymers without any improvement in the storage modulus, loss modulus or complex viscosity. In a second part, the viscoelastic characteristics were investigated using dynamic mechanical thermal analysis (DMTA). DMTA spectra showed an increase in the storage modulus with the increase of poly(lactic acid) content but the opposite was observed for the loss modulus. A cold crystallization of poly(lactic acid) is observed around 87–100 °C and the temperature of glass transition of poly(lactic acid) did not depend on the composition of the blend. These results indicate that LDPE and PLA are immiscible in all proportions either in the melt state or in the solid state.

Keywords Polyethylene · Poly(lactic acid) · Rheology · Viscoelastic properties · Polymer blends · Die swell

Introduction

Polymer rheology has attained a key position in polymer research, being an important link between the production of polymers and their end-use properties [1]. The rheological behaviour of molten polymers is of great importance in understanding the flow behaviour of these materials during processing, to optimize the processing conditions and to define the most suitable application fields [2–4].

Studies related to rheological behaviour of pure polymeric melts are well documented, while such studies on molten polymer blends are relatively limited, but are indispensable [5]. The present work deals with rheological characteristics of low-density polyethylene (LDPE) and poly(lactic acid) (PLA) blend. This blend has recently received an increasing attention and several studies on polylactide and polyethylene blends have reported mechanical and morphological characteristics [6–9]. However, very limited researches on rheological behaviour of LDPE/PLA blend exist in the literature [10–12]. Yomogida and coworkers [10] focused on the influence of the shear condition on the properties of compatibilized LDPE/PLA blend. They pointed out that the application of high-shear conditions positively affected the morphology of the blend system. The authors also found that the blends obtained by the combination of reactive blending and high-shear processing exhibited an excellent improvement in the mechanical properties.

In the work of Jiang et al. [11], blends of polylactide and linear low density polyethylene (LLDPE) were produced at different intensities using different screw configuration. The authors showed that high shear/chaotic mixing led to strong interactions between minor polymer and matrix which result in a decrease in the crystallinity of blends. More recently, As'habi et al. [12] studied the rheological behaviour of two different PLA/LLDPE (75/25) nanocomposite systems based on two different kinds of nanoclays. They found that PLA/LLDPE nanocomposites had a typical non-Newtonian behaviour with a shear thinning behaviour. They also showed that, by increasing the nanoclay contents, the complex viscosity of PLA/LLDPE blend increased monotonically.

Like most polymer blends, low density polyethylene and poly(lactic acid) are immiscible and their rheological behaviour is generally complex depending strongly on morphology, composition, viscoelastic properties and the state of the interface between the components [13–15]. Thus, knowledge of melt behaviour of this blend is important.

In this paper, the rheological and the viscoelastic characteristics of low density polyethylene (LDPE)/poly(lactic acid) (PLA) blends are investigated to help to understand the influence of each polymer on the flow behaviour and the viscoelastic properties of the other. Data were obtained using capillary rheometer, melt indexer (steady shear mode), parallel-plates rheometer (dynamic shear mode) and dynamic mechanical thermal analyser (DMTA).

Experimental

Materials

Low-density Polyethylene (LDPE 1003/FE/23), with a density of 0.923 and a melt index of 0.3 g/10 min, was obtained from Total Petrochemicals, Belgium. The poly(lactic acid), PLA L9000, was purchased from Biomer® (Germany) and had a molecular weight of about 200,000 g/mol, a density of 1.25 and a melt index of 3–6 g/10 min. The melt temperatures of these two polymers were 111 and 168–172 °C, respectively.

Melt blending and preparation of test specimens

Blends which contain low density polyethylene and poly(lactic acid) were prepared from the components in the entire composition range from 0 to 100 wt% using a twin-screw extruder. PLA20, PLA50 and PLA80 correspond to LDPE/PLA 80/20, LDPE/PLA 50/50 and LDPE/PLA 20/80 in weight, respectively. Before being extruded, all polymers were dried under vacuum at 80 °C for 24 h to remove water and other volatile components. The produced extrudates were cooled in air and pelletized immediately after blending. The pellets were used as they are (in MFI measurements and capillary rheometry) or moulded by compression at 180 °C using a laboratory press into discs (1 mm thick, 25 mm diameter) and plates of 4 mm thickness. Discs and plates, destined for parallel-plates rheometery and DMTA, respectively, were slowly cooled down to room temperature. Before conducting the experiments, samples were vacuum-dried at 80 °C for 24 h.

Melt flow index (MFI)

MFI measurements of LDPE/PLA blends were done on pellets using a melt indexer (MELT Flow Rate Apparatus, Model 5/SF 12) by applying a standard weight of 2.16 kg at a melt temperature of 190 °C, in accordance with ASTM 1232–82. MFI (in g/10 min) is the rate of extrusion of the sample which is under the pressure of the

dead load through an orifice. For each formulation, at least 6 extrudates were cut at regular intervals and weighed; the average value is then reported.

The melt flow index is obtained using the equation below:

$$\text{MFI} (190\,^\circ\text{C}) = \frac{600 \cdot m}{t}, \tag{1}$$

where MFI is the Melt Flow Index (g/10 min), m mass extruded (g) and t time required to the extrusion of the mass m (s).

Steady-state shear mode (Capillary rheometer)

All the data quoted here were obtained using a capillary rheometer manufactured by CONTROLAB (Model 102, Cop 10, maximal Pressure 300 kg/cm^2). The length to radius ratio of the capillary (L/R) was 54; thus the end effects may be quite small and the Bagley correction for shear stress is negligible [16]. The rheology experiments were carried out at different temperatures (180, 190 and 200 °C) in a range of pressure where melt flow instabilities, ex. melt fracture, are avoided. Before each measurement, samples in form of pellets were preheated for 5 min at the desired temperature to obtain a uniform temperature.

The rheological measurements were performed in triplicate and the results reported were an average of these measurements.

The extrudate swell was measured as the ratio of the diameter of the extrudate to the diameter of the capillary. At least ten extrudates were carefully collected from the capillary die and their diameters were measured using a microscope.

Dynamic shear mode (Parallel-plate rheometer)

Dynamic rheological measurements were conducted on an ARES parallel-plate rheometer (RHEOMETRIC SCIENTIFIC, LN2) using a disc of 25 mm of diameter and a gap of about 1 mm. A small strain of 5 %, determined in preliminary tests, was employed to maintain the measurements within the linear viscoelastic region where all polymers remained stable. Frequency sweeps were performed over the range of 10^{-1} to 10^2 (rad/s) at a temperature of 175 °C. All tests were conducted with nitrogen as the heating medium to avoid degradation during testing. The software TA Orchestrator data analysis was used to obtain the experimental data and to calculate the different dynamic shear properties like storage modulus (G′), loss modulus (G″) and complex viscosity (η*). Before the measurements, samples are kept at the initial temperature for 3 min. The results reported are an average of three measurements performed on previously vacuum-dried samples. In general, a good reproducibility was obtained for all formulations.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical properties of LDPE/PLA blends and their components were studied in compression mode with a VA 815 Metravib RDS apparatus. The storage Modulus (E′), loss modulus (E″) and loss factor, tan δ, were measured at a

constant frequency of 5 Hz and heating rate of 3 °C/min. Specimen used, in form of bars with dimensions of $40 \times 10 \times 4$ mm^3, were cut from the plates.

## Results and discussion

Capillary rheological properties

Melt flow index (MFI)

The melt flow index (MFI) is the most common test used in polymer industry and occasionally the only rheological information used [17, 18]. The quality of nearly every batch of thermoplastic made in the world is controlled by melt index and rheologists are often asked to compare their results to melt index values [17]. It is indicative of the flow characteristics and, therefore, the processing ability of the molten polymer.

The MFI values of LDPE, PLA and their blends are shown in Fig. 1. LDPE has an MFI of 0.3 ± 0.05 g/10 min; however, PLA has an MFI of 5.9 ± 0.08 g/10 min which are very close to values found for non-extruded pellets. This measurement was undertaken to check any degradation of polymers when being extruded. As found, both extruded materials present the same rheological characteristic as raw materials, indicating the absence of structural changes in LDPE or PLA. Therefore, it can be deduced that the process used here was adequate in terms of preserving the molecular structure of materials.

The results of MFI revealed also that LDPE had a molecular weight and melt viscosity greater than those of PLA since the melt index was inversely related to the molecular weight and viscosity. In addition, Fig. 1 showed that the incorporation of PLA leads to an increase in the MFI of the blends. The increase in the melt index of the blends indicates that the presence of PLA facilitates the processing of the

Fig. 1 Melt flow index of LDPE, PLA and their blends
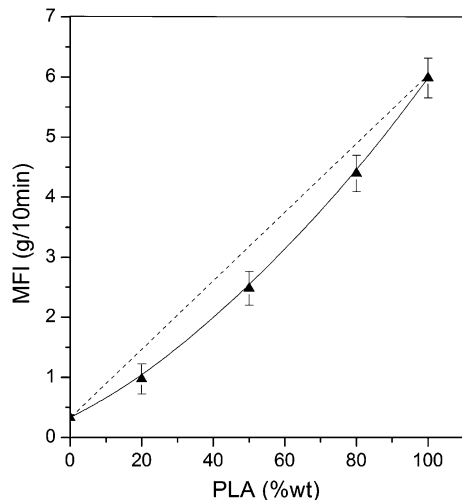
melting blends. However, values of the MFI of blends were lower than those predicted by the additivity law (dashed line) which may indicate the immiscibility of the two components in the melt.

Steady shear flow

Measurement of flow curves within a wide range of shear rates and melt temperatures allows the collection of information necessary for the selection of the
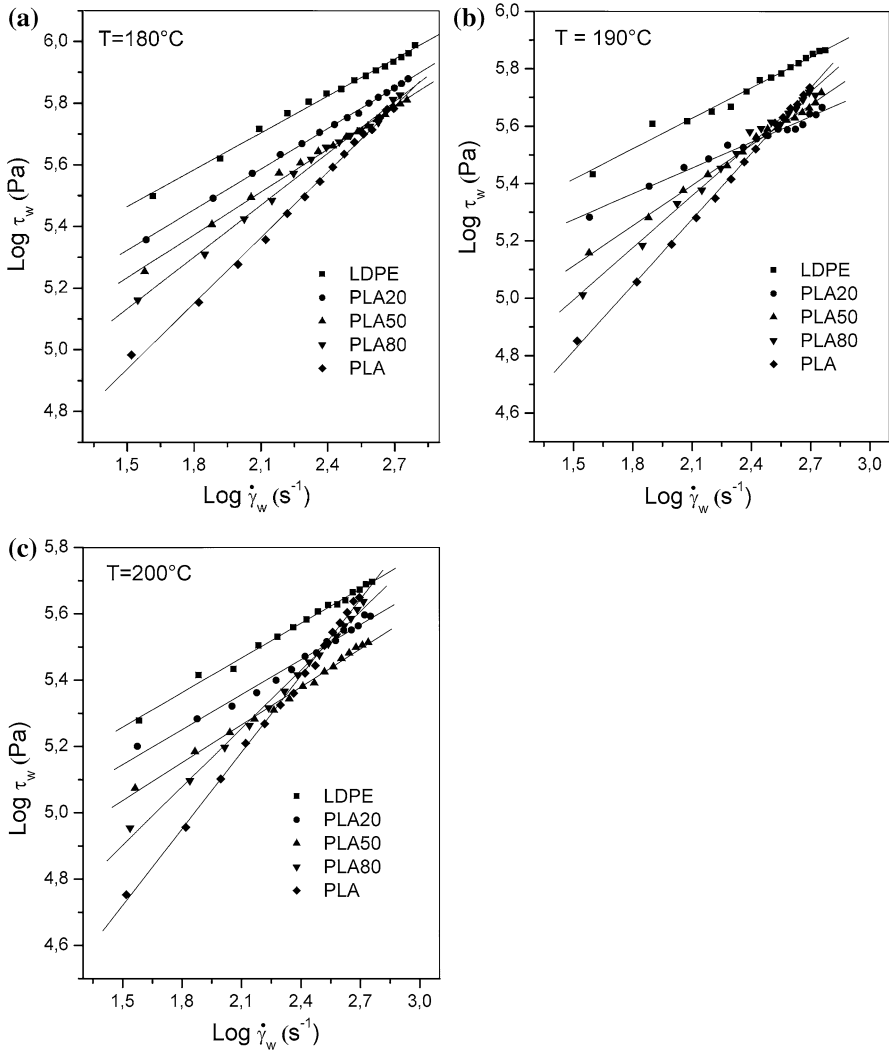

Fig. 2 Logarithm plots of shear stress vs. real shear rate for LDPE/PLA blends at: **a** 180 °C, **b** 190 °C, **c** 200 °C

most appropriate conditions to transform the polymer into qualitatively and economically valid manufactured items [3].

The effect of shear rate on shear stress of LDPE, PLA and their blends measured in the capillary rheometer at 180, 190, and 200 °C is shown in Fig. 2. For each temperature, the expressions used to relate pressure drop ΔP (pressure difference between the entrance and exit of the capillary) to shear stress τ_w, and volume flow rate Q to apparent shear rate at the wall $\dot{\gamma}_{aw}$ in a capillary of radius R and length L are as follows [16, 17]:

$$\tau_w = \frac{\Delta P \cdot R}{2L} \tag{2}$$

$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3}, \tag{3}$$

where both τ_w and $\dot{\gamma}_{aw}$ apply at the capillary wall.

Due to high L/D ratio used in this study, the Bagley correction commonly used to correct the shear stress is not necessary for the first equation [16]. However, Eq. (3) was corrected using the Rabinowitsch correction according to the following equations:

$$\dot{\gamma}_w = \frac{1}{4}\left(3 + \frac{d\log\dot{\gamma}_{aw}}{d\log\tau}\right)\dot{\gamma}_{aw} \tag{4}$$

$$\dot{\gamma}_w = \dot{\gamma}_{aw}\left(\frac{3n+1}{4n}\right), \tag{5}$$

where $\dot{\gamma}_w$ is the true shear rate at the wall and n is the flow index.

Figure 2 shows linear variation of shear stress (τ_w) versus shear rate ($\dot{\gamma}_w$) over the entire shear rate studied and all temperatures, confirming the validity of the power–law relationship for these samples. The power law is given as follows:

$$\tau_w = K\dot{\gamma}^n, \tag{6}$$

where K is the consistency index and n is the power–law index (or flow index).

Table 1 Values of power–law index (n), consistency index (K) and correlation coefficient (R^2) obtained from shear stress versus shear rate plots

		PLA (wt%)	0	20	50	80	100
180 °C	n			0.45	0.50	0.56	0.69	0.75
	R^2			0.977	0.992	0.992	0.996	0.996
	K (Pa.s^n) 10^3		71.64	34.88	19.02	9.77	4.99
190 °C	n			0.49	0.55	0.59	0.69	0.77
	R^2			0.974	0.997	0.996	0.998	0.998
	K (Pa.s^n) 10^3		42.24	24.26	11.95	6.17	3.10
200 °C	n			0.54	0.58	0.62	0.73	0.81
	R^2			0.993	0.995	0.992	0.993	0.998
	K (Pa.s^n) 10^3		28.20	12.15	9.24	3.55	2.14

Values of n, K, and the correlation coefficient (R^2) obtained from these straight lines are listed in Table 1. The table reveals high correlation coefficients ($R^2 > 0.97$). For the three temperatures, the values of the power–law index are lower than unity ($n < 1$) indicating that all blends and their components exhibited pseudoplastic (non-Newtonian) behaviour. However, the n values increased as PLA concentration increased and for each formulation they increased with increase in temperature. The value of n describes the deviation of the flow behaviour from the Newtonian fluids behaviour. A high values of n reveal less influence of shear rate on flow behaviour [19], so it could be said that the flow behaviours of PLA and PLA-rich blend are less sensitive to shear rate compared to LDPE and LDPE-rich blend.

The consistency index decreases with the increase in PLA concentration and for the same formulation it decreases with the increase in temperature. This means that
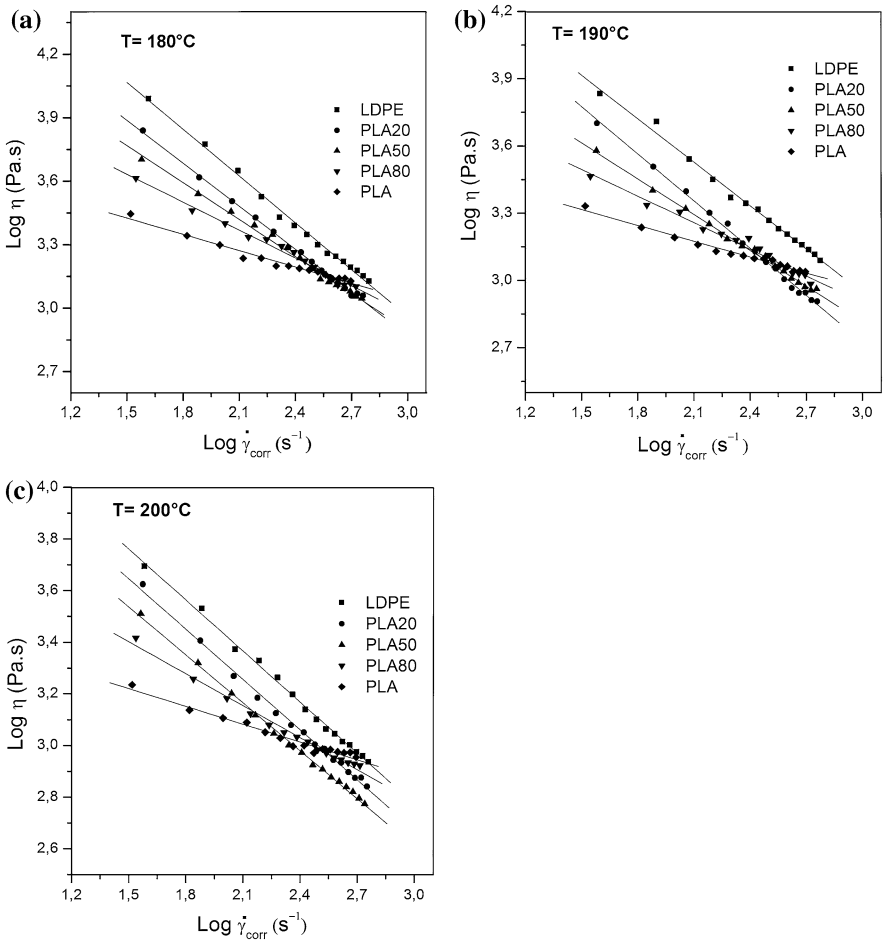

Fig. 3 Logarithm plots of melt viscosity vs. corrected shear rate for LDPE/PLA blends at: **a** 180 °C, **b** 190 °C, **c** 200 °C

the resultant materials required less force to flow. These observations may be attributed to the fact that PLA is less viscous (MFI ∼ 6 g/10 min) than LDPE (MFI ∼ 0.3 g/10 min), so its incorporation increased the flowability of the blends. Also, the rise in temperature leads to a decrease of the consistency index, but PLA seems to be less affected by the temperature variation compared with LDPE or the rest of blends.

The true shear viscosity (η) of the different compositions was calculated as follows:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}, \tag{7}$$

where τ_w and $\dot{\gamma}_w$ are the shear stress and true shear rate, respectively.

The dependence of the true shear viscosity on the true shear rate, depicted in Fig. 3, shows a linear variation. Slopes of theses curves are quite consistent with the power–law relation:

$$\eta = K(\dot{\gamma}_w)^{n-1}, \tag{8}$$

with values of n consistent with those shown in Table 1.

It can be seen from Fig. 3a, b and c that with increasing shear rates, the viscosity of LDPE, PLA and their blends decreased, indicating a shear thinning behaviour for all formulations. Pure LDPE had higher viscosity than either pure PLA or blends in all ranges of the shear rates and temperatures. However, for all formulations, the dependence of the melt viscosity on shear rates was different as temperature varies, mainly for the blends. These results may indicate that the optimal processing conditions for neat polymers or blends could be quite different [20].

At low and moderate shear rates, LDPE and blends exhibited higher viscosities than PLA, but at high shear rates, the flow curves had the tendency to converge or to intercross. The cross point shifted to lower shear rates with increase in temperature. This result can be related to the fact that at low and moderate shear rates, long and flexible macromolecular chains of LDPE can entangle among themselves and also with PLA chains hindering the flow of the melt and consequently the viscosity became higher. However, at high shear rates, LDPE macromolecular chains in the blends tend to disentangle and align leading to a slippage between the chains, decreasing thus the viscosities. This kind of behaviour may be observed with blends made up of incompatible polymers as a result of the weakness at the planes between the interfaces [21].

From these figures, it can be concluded that below the cross point, PLA is the less viscous component, whereas above this cross point the LDPE is the less viscous. Furthermore, at low shear rate the influence of PLA on the behaviour of the blends is clearly visible, but at high shear rate, LDPE has more influence.

To evaluate the effect of temperature on melt viscosity at specified shear rate, plots of the true viscosity against the reciprocal of temperature ($1/T$) were made. Figure 4, which shows these plots at two shear rates, reveals a group of straight lines, indicating that the relationship between the true viscosity and temperature follows Arrhenius equation [Eq. (9)]:

$$\eta = Ae^{\Delta E_\eta/\mathrm{RT}}, \qquad (9)$$

where η is the melt viscosity (Pa.s), ΔE_η the flow activation energy (J/mol), A a constant (Pa.s), T the absolute temperature (K) and R the gas constant (8.3144 J/mol.K).

The flow activation energies of homopolymers and blends can be calculated from the slopes of these lines. Table 2 shows the different values of ΔE_η obtained, at the two shear rates (40 and 200 s^{-1}), with high correlation coefficients ($R^2 \geq 0.99$).

The activation energy of flow is the minimum energy required for the macromolecular chains to just flow which is equivalent to energy necessary to overcome the intermolecular forces of attraction as well as the resistance due to the entanglements [22].

As seen in Table 2, at low shear rate ($\dot{\gamma}_{\mathrm{corr}} = 40$ s^{-1}), pure PLA possessed higher flow activation energy (66.89 kJ/mol) than pure LDPE (48.32 kJ/mol). This may be due to the strong intermolecular forces in PLA owing to its polar nature which provides higher rigidity of macromolecular chains and relatively greater resistance to flow compared to those of LDPE. Similar results were obtained for blends of polar polymers with non-polar polymers such as thermoplastic polyurethane and ethylene–propylene–diene elastomer (TPU/EPDM) studied by Wang and Luo [23], linear low density polyethylene and polycarbonate (LLDPE/PC) studied by Utracki and Sammut [24] and low density polyethylene blended with polystyrene (LDPE/PS) studied by Xu et al. [25]. For all cited blends, polar polymers had greater flow activation energies than non-polar polymers.

For the blends, the activation energy increased with increasing PLA content. However, 80/20 and 20/80 (LDPE/PLA) compositions exhibited elevated activation energy than 50/50 LDPE/PLA composition. This result may be attributed to differences in the morphology of these blends. It is well known that the rheological
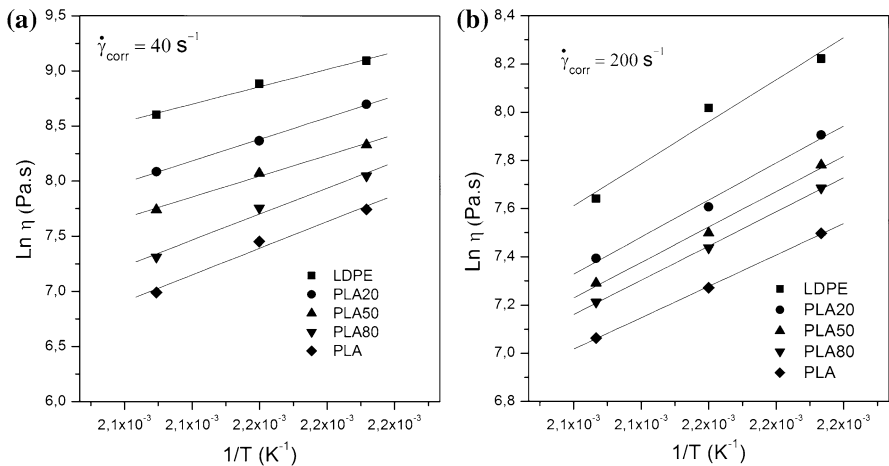

Fig. 4 Plots of Ln η versus 1/T for LDPE, PLA and their blends at: a ($\dot{\gamma}_{\mathrm{corr}} = 40$ s^{-1}), b ($\dot{\gamma}_{\mathrm{corr}} = 200$ s^{-1})

Table 2 Dependence of activation energy (ΔE_a) with composition for viscous flow of LDPE/PLA blends

PLA (wt%)		0	20	50	80	100
Activation energy ΔE_a (kJ/mol)	Shear rate = 40 s^{-1}	48.32	54.61	52.34	65.35	66.89
	Shear rate = 200 s^{-1}	43.68	42.57	40.70	39.29	36.07

behaviour of multiphase polymer systems is intimately related to their morphology [26].

At high shear rate ($\dot{\gamma}_{corr} = 200$ s^{-1}), the activation energy decreased with addition of PLA, and the greater the content of PLA, the lower the activation energy. This result implies that the presence of PLA facilitates the processing of the melting blends.

Table 2 shows also the decrease of activation energy for each composition with the increase of the shear rate. This may be attributed to the greater destruction of entanglement and intermolecular interactions between chain segments under high shear, which results in a decrease in viscosity and, hence, ΔE_η becomes smaller as shear rate increases [27]. For the blends, the variation of ΔE_η could be attributed to the change in the morphology under shear deformation. In general, if the two polymers in a blend are rheologically different, the flow on each side of the interface is different and, therefore, the interaction of the overall flow with the interface is more complex [28].

Moreover, at low shear rate, PLA and compositions with droplets/matrix morphology are more sensitive to processing temperature than LDPE and 50/50 composition since the higher the ΔE_η, the higher the sensitivity [27, 29]. However, at high shear rate, LDPE is more sensitive to temperature.

Melt elasticity

One of the classic methods used to characterize the melt elasticity of polymers is the extrudate swell. The viscoelastic fluid, flowing through a capillary, gives rise to diameter of extrudate which is considerably higher than the diameter of the capillary, at the die exit [30, 31]. The extrudate swell, also called die swell or the Barus effect, occurs as a result of the recovery of the elastic deformation imposed during processing of a polymeric material [32]. This intrinsic melt property influences finished products' performance and plays a vital role in product and die designs, as well as on process controls [33].

Die swell is measured by determining the diameter of the extruded strand (D_e) after it has exited the capillary die and data are usually presented as a ratio (D_e/D), where D is the diameter of the die.

Variations of swelling ratio with LDPE/PLA blend composition, for three different shear rates, are depicted in Fig. 5. For homopolymers, LDPE presents high swelling ratio than PLA for all shear rates. This may be attributed to the presence of long-chain branching in LDPE which contributes significantly to its high melt elasticity [34].

Fig. 5 Swelling ratio of LDPE/PLA blends as function of PLA content and shear rates
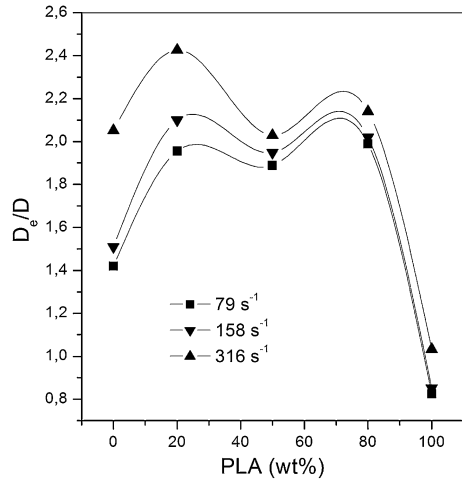
For the blends, the die swell increases with increase in PLA content until 20 % and then decreases gradually. However, values corresponding to blends are higher than those of the homopolymers for all shear rates. Similar observations were made by Acierno et al. [35] and Liang and Ness [36] who studied, respectively, the flow properties of blends of low density polyethylene/linear low density polyethylene, and low density polyethylene/polypropylene and observed that the blends always had a larger die swell than the parent polymers.

Results of extrudate swell of LDPE/PLA blends may be explained in terms of morphology where the swelling ratio of blends with well-dispersed morphology (80/20 and 20/80 LDPE/PLA) is greater than that of the hompolymers and the blend with co-continuous morphology (50/50 LDPE/PLA). However, blends with PLA dispersed phase have greater swelling ratio than that of blends with LDPE dispersed phase. As known, the greater the extent of drop deformation inside the die, the larger will be the extrudate swell [34, 37]. Thus, since the viscosity of LDPE is higher than that of PLA, the PLA droplets will be subjected to higher deformation than LDPE droplets, and will exhibit larger extrudate swell.

Furthermore, for all formulations, the D_e/D ratios increase as the shear rates increase which is in concordance with the results found in the literature [38, 39]. This effect is larger for LDPE and LDPE-rich blend but negligible for PLA. This observation may be explained by the fact that the higher the extrusion rate, the greater the deformation of the macromolecule chains inside the die and the higher will be the shear deformation energy stored in the polymer melt, leading to a corresponding increase in the swelling of the extrudate [32].

Dynamic rheological properties

Results from dynamic rheological study are shown in Figs. 6 and 7. Figure 6a, b and c show, respectively, the storage modulus, the loss modulus and the complex viscosity of homopolymers and blends as a function of angular frequency at 175 °C.

In Fig. 6a, one can see that the storage modulus increases with increasing frequency for all compositions. This can be explained by the fact that at low frequencies macromolecular chains can rearrange but, as the frequency increases, they have less time to relax [40]. The neat LDPE and blends had higher storage moduli than PLA except for very high frequency. Values of the storage moduli of blends increased with LDPE content and lie between the values of the homopolymers. This result indicates that LDPE is significantly more elastic than PLA and the blend becomes further elastic with the incorporation of LDPE.

Figure 6b shows that the variation of loss moduli is similar to that of storage moduli at low frequencies (<10 s^{-1}), but for frequencies higher than 10 s^{-1}, values of loss modulus are inverted and PLA exhibits higher values than LDPE and blends. The blend with 20 % PLA exhibits a high value of storage modulus. In general, the blends with droplet/matrix morphology should display a higher interfacial area, and in turn an excess of elasticity, while a co-continuous phase morphology has a lower interfacial area [41].
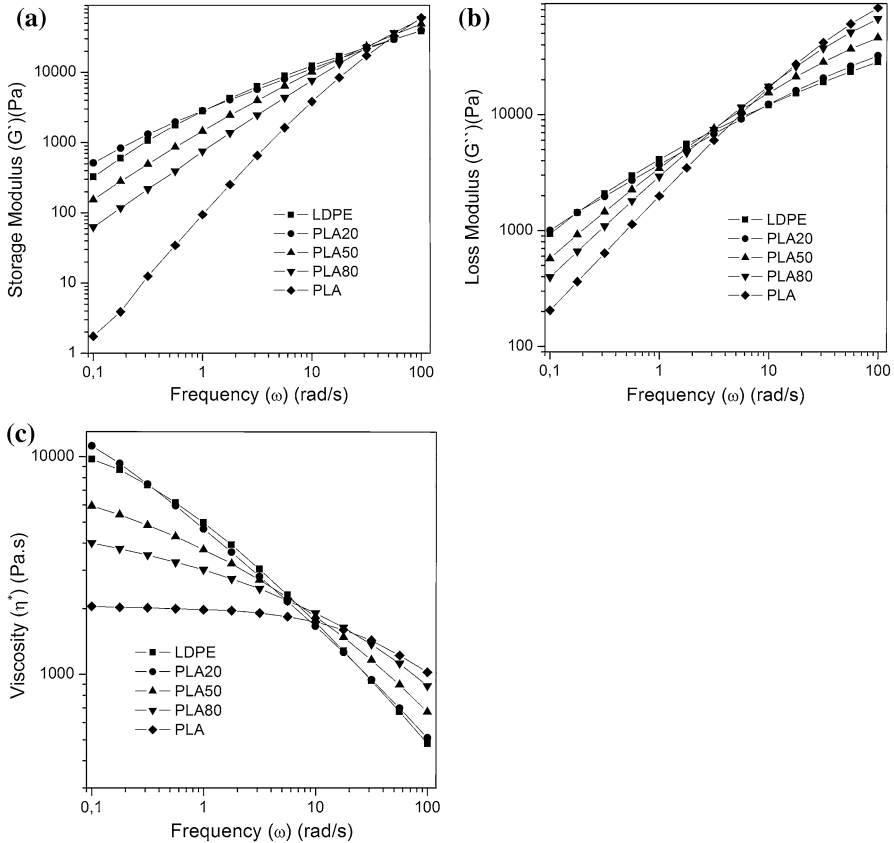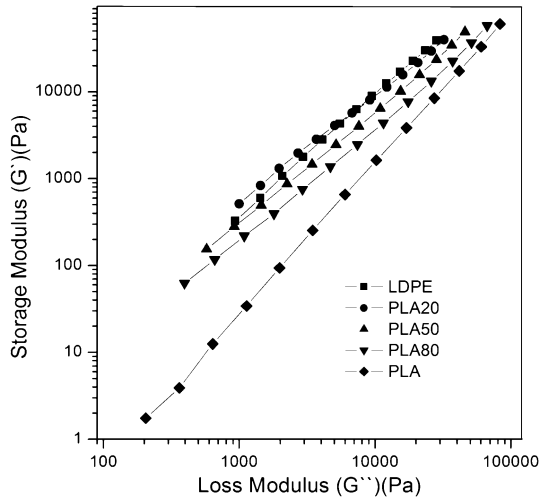

Fig. 6 Dynamic rheology: a storage modulus, b loss modulus, c complex viscosity as a function of frequency for LDPE/PLA blends ($T = 175$ °C)

Fig. 7 Storage modulus (G′) as a function of loss modulus (G″) of LDPE/PLA blends

From these results, one can also observe for each formulation (LDPE, PLA, blends) that the loss modulus is higher than the storage modulus, thus the energy dissipated is higher than the stored energy, especially at low frequencies.

In Fig. 6c, all formulations demonstrate shear thinning behaviour and only virgin PLA which exhibits a clear Newtonian plateau. LDPE and the other blends do not exhibit such plateau and their viscosities follow power–law behaviour. However, the variation of the complex viscosity is strongly dependent on the frequency: at low frequencies (<10 s^{-1}), pure LDPE and blends had higher viscosities than pure PLA, but at frequencies higher than 10 s^{-1} PLA is the most viscous. From the above data, it can be concluded that each continuous phase controls the properties of the blend.

The log plots of storage modulus (G′) versus loss modulus (G″), as reported in Fig. 7, are very useful tool to interpret the rheological behaviour of compatible and incompatible polymer blends [37, 40]. Some authors [42, 43] reported that when a blend system is compatible on the molecular level, it gives rise to temperature-independent and composition-independent correlations when G′ is plotted against G″. Therefore, as long as the molecular structure is kept the same, the ratio of the energy stored and the energy dissipated during the shear deformation is expected to be independent of the blend composition [37]. In this study, as can be seen from Fig. 7, the variation of storage modulus (G′) with loss modulus (G″) depends on the composition of the blends confirming thus the incompatibility of our blend (LDPE/PLA) in all proportions.

DMTA analysis

Dynamic thermomechanical analysis (DMTA) tests are very useful to evaluate the viscoelastic characteristics as well as other properties such as phase separation (in multicomponent systems), effects of specific processing treatment, stiffness and its variations with temperature, degree of crystallinity, etc. [44]. Plots of storage

modulus (E′), loss modulus (E″) and loss tangent (damping) as function of temperature, provided by DMTA for LDPE/PLA blends, are shown in Fig. 8a, b and c, respectively. The storage modulus (E′) describes the elastic energy stored that can be subsequently restituted while the loss modulus (E″) describes the energy dissipated during the viscous flow.

Figure 8a reveals a drop in the storage modulus of pure PLA and the different blends around 70 °C. This drop, which becomes less pronounced with the increase of LDPE content, is accompanied by the appearance of maxima in loss modulus and tan δ, as shown in Fig. 8b and c, respectively. No drop occurs for pure LDPE. These changes in curves can be associated with the α-relaxation processes related to the glass transition of the amorphous phase of PLA [45]. In addition, E′ and E″ of LDPE and 80/20 LDPE/PLA blend showed a drastic decease around 100 °C which can be attributed to the melting of LDPE crystalline phase. For 50/50 and 20/80 LDPE/
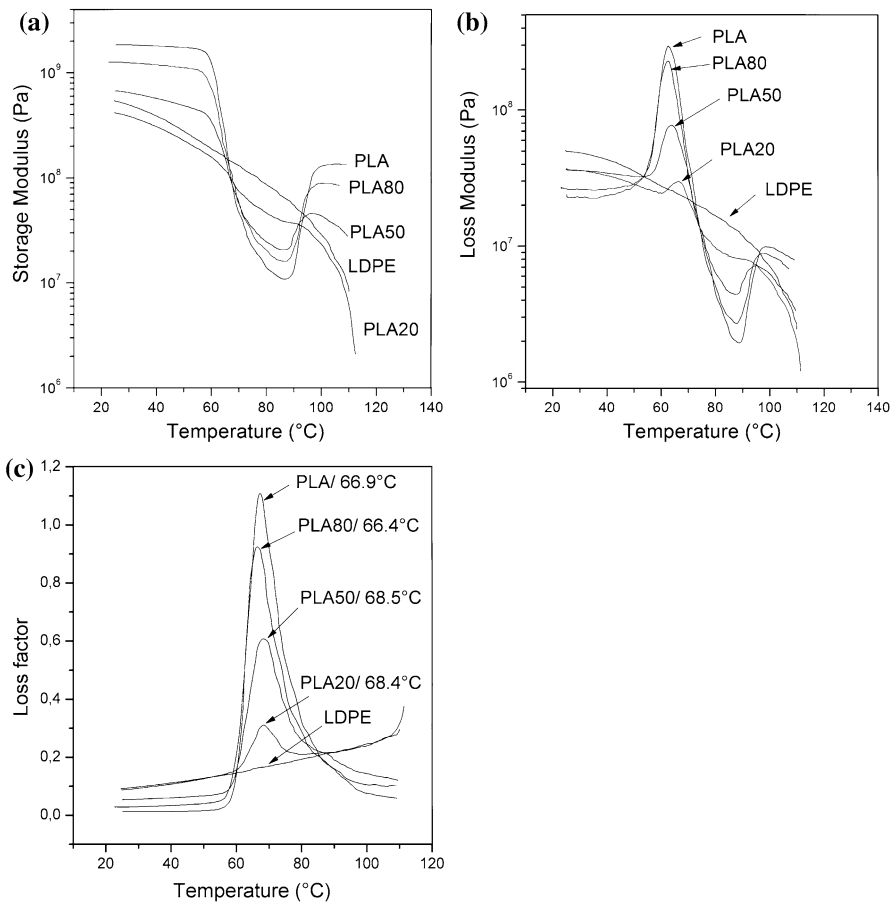

Fig. 8 DMTA thermograms of LDPE, PLA and their blends: **a** storage modulus, **b** loss modulus, **c** loss factor (tan δ)

PLA blends and pure PLA, this stiffness decrease is compensated by the strengthening due to the presence of the crystalline phase of PLA.

The temperature of glass transition (T_g) is commonly assigned to the peak value of the damping factor, or to the peak value of the loss modulus, or to the onset of the drop of the storage modulus [46]. However, T_g is usually determined as the temperature at which tan δ attains its maximum [47]. In this study the maximum of tan δ is chosen. Using Fig. 8c, one can observe that neat PLA had a T_g of 66.9 °C, whereas those of the blends ranged between 68.4 and 66.4 °C. The T_g of PLA measured here did not depend on the composition of the blend and no shift was observed, indicating that this blend system is immiscible.

Before the glass transition of PLA, i.e. in the glassy state, the storage moduli of blends and LDPE (Fig. 8a) are lower than that of the PLA. For the blends, this modulus decreased with increase in LDPE content which could indicate a small plasticizing effect of PLA amorphous phase since the LDPE is in the rubbery state. After the glass transition, the neat PLA exhibited maximum drop in storage modulus and highest peaks for loss modulus and Tan δ (Fig. 8b and c).

As the temperature increases, in the region from 87 to 100 °C, an increase in the storage and loss moduli of pure PLA and blends is observed (Fig. 8a and b). This reflects an increase in the materials stiffness. Similar observations were made by Pluta [48], Pluta et al. [49] and Ren et al. [45] who attributed this increase to the cold crystallization in the PLA phase. This phenomenon may be explained by the fact that upon heating above T_g, macromolecular chains gain enough mobility to rearrange into crystallites, which causes a dramatic increase in modulus [50].

Conclusion

In this work, rheological and viscoelastic properties of low density polyethylene/poly(lactic acid) blends were investigated. Melt flow index (MFI) measurements revealed that LDPE had a molecular weight and melt viscosity greater than those of PLA and that the incorporation of PLA leads to an increase in the MFI of blends. Capillary rheology showed that homopolymers as well as LDPE/PLA blends exhibited typical pseudoplastic flow behaviour. However, this behaviour was less emphasized for PLA which had high values of power-law index ($n = 0.75$–0.81). Results also indicated a shear thinning behaviour for LDPE, PLA and their blends and a decrease in the consistency when the content of PLA increased. Pure LDPE had highest viscosity than either pure PLA or blends in all ranges of shear rates and temperatures. The effect of temperature on viscosity of mixtures and homopolymers was well described by Arrhenius relationship with high correlations (R^2). Furthermore, PLA showed higher activation energy than LDPE and blends but lower melt elasticity. For blends, activation energy and melt elasticity were greatly dependent on morphology. For all formulations, activation energy varied inversely with shear rate but the melt elasticity varied proportionally with it.

The investigation of dynamic rheological properties showed that neat polymers and their blends demonstrated shear thinning behaviour and only virgin PLA

exhibited a clear Newtonian plateau. No improvement in the storage modulus, loss modulus and complex viscosity is observed for blend.

Dynamic mechanical thermal analysis revealed no influence of the blend composition on glass transition temperature. DMTA results showed also a small plasticizing effect of amorphous PLA phase due to the presence of LDPE which is in the rubbery state. In the temperature range 87–100 °C, an increase in the storage and loss moduli of pure PLA and blends related to the cold crystallization in the PLA phase is observed.

Based on results obtained by capillary rheology, dynamic rheology and DMTA, it may be concluded that LDPE and PLA are immiscible either in the melt state or in the solid state.

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