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Processing Aids for Biodegradable Polymers

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ABSTRACT: The melt fracture behavior of several commercial polylactides (PLAs) and poly(ε-caprolactone) (PCL) is investigated. PLAs and PCL with molecular weights greater than a certain value were found to exhibit melt fracture phenomena in capillary extrusion, which manifests itself as distortions on their surface once the extrusion rate exceeds a critical value. It was found that the addition of a small amount of PCL (typically 0.5 wt %) into the PLA and vice versa is effective in eliminating and delaying the onset of melt fracture to higher shear rates in the capillary extrusion of PLA and PCL, respectively. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3592–3600, 2013

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INTRODUCTION

Biodegradable polymers such as polylactide (PLA) and poly (ε-caprolectone) (PCL) have attracted an increasing amount of attention over the last decades, due to environmental concerns.[1,2] Their rheology has been extensively studied in the literature, i.e., for PLAs see Refs. 3–7 and for PCLs see Refs. 8–12.

Although the rheology of PLAs has been well documented in the literature, their processing as can be assessed by melt fracture phenomena[13–16] has not been studied with the exception of a few recent publications.[12,17,18] During extrusion and when the wall shear stress exceeds a certain value, molten polymers exhibit certain flow instabilities collectively known as melt fracture (surface distortions on extrudates). These can be small amplitude periodic distortions known as sharkskin melt fracture,[13,14,16,19] alternate distorted, and relative smooth portions, known as stick-slip or oscillating melt fracture[15,20] and gross irregular distortions known as gross melt fracture.[21]

To overcome these difficulties and to render the processes economically feasible, polymer processing aids (PPAs) are frequently used. PPAs can eliminate the flow instabilities known as sharkskin melt fracture and stick-slip, or postpone them to higher flow rates. The end result is an increase of the productivity as well as an energy cost reduction, while high product quality is maintained.[22–29]

The main objective of this article is to examine first the melt fracture phenomena occurring in the extrusion of PLAs and PCL and second identify appropriate processing aids that can enhance their processability. The geometric factors of the dies that play a role in the effectiveness and the time required (induction time) to eliminate melt fracture phenomena are also examined. Finally, the mechanisms by which the identified processing aids work effectively will also be discussed.

MATERIALS AND METHODS

Three commercial PLAs were studied in this work all obtained from NatureWorks LLC (Minnetonka, MN). These are listed in Table I. These commercial samples have different molecular weights and about the same polydispersity (Table I). A commercial poly(ε-caprolactone) (PCL) polymer was also used which was obtained from Perstorp Polyols Inc. (Toldeo, OH) (Capa® technology). Some physical properties and molecular characteristics of this polymer are also summarized in Table I. Most of these properties and detailed rheological characterization can be found in Othman et al.[18] for PLAs and in Noroozi et al.[12] for PCL.

A fluoropolymer (PA 5951) that was provided by Dyneon was also tested as a possible processing aid for PLAs and PCLs. It is known that fluoropolymers such as PA 5951 are very effective in eliminating sharkskin and oscillating melt fracture in the extrusion of polyethylenes. Some of the typical properties of this polymer are: surface area of 10 $m^2\ g^{-1}$, a density of 350 $g\ L^{-1}$, a particle size of 6 μm, and a melting temperature of 130°C.

The processability and shear viscosity at high apparent shear rates where polymers exhibit melt fracture were studied by using a pressure driven Instron capillary rheometer equipped with a barrel having a diameter of 0.9525 cm. Three series of dies having a fixed diameter and various length-to-diameter ratios were used to

Table I. Molecular Characteristics and Other Properties of the PLAs and PCL Used in this Work

Sample	M_w (kg mol^{-1})	M_w/M_n	T_g (°C)	T_m (°C)	η_o (Pa s) at 160°C
PLA7001D	110.1	1.59	57.1	149.0	21,000
PLA2002D	106.9	1.82	56.5	152.4	17,200
PLA3251D	55.4	1.62	58.8	167.9	1000
PCL6800	88.4	1.22	−60	55	3163

address the effects of the geometrical characteristics of die on melt fracture and the effectiveness (induction time) of processing aids.[13,14] All dies had an entry angle of 180°. These are summarized in Table II along with their characteristic dimensions. The extrudates from the capillary extrusion experiments were inspected by Olympus MIC-D microscope to detect any visual defects known as melt fracture phenomena.

RESULTS AND DISCUSSIONS

The Flow Curves and Melt Fracture of PLAs

The capillary rheometry of all commercial PLAs and PCL has been studied to assess possible melt fracture effects. The raw data obtained from such a piece of equipment (pressure drop, Δp versus volumetric flow rate, Q) can be transformed into fundamental rheological data (shear stress and shear rate) by the following two equations. First, the apparent wall shear stress is given by:

$$\sigma_{w,a} = \Delta p / 4(L/D) \quad (1)$$

where $\sigma_{w,a}$ is the apparent shear stress, L/D is the length-to-diameter ratio of the capillary die, and Δp is the total pressure drop. The apparent shear rate is given by:

$$\dot{\gamma}_A = 32Q/\pi D^3 \quad (2)$$

where Q is the volumetric flow rate. The relationship between the apparent shear stress versus apparent shear rate is known as the apparent flow curve. To obtain the true shear stress along the capillary wall and the true shear rate to determine the flow curve and the shear viscosity of polymers, the Bagley and Rabinowitch corrections should be applied.[30]

Figure 1(a, b) plot the apparent flow curves of PLA7001D and PLA2002D, respectively, at three temperatures, namely 180°C, 200°C, and 220°C. The degree of drop in the wall shear stress scales according to the time–temperature superposition obtained

Table II. Characteristic Dimensions of Capillary Dies Used

Diameter (mm)	L/D	Entry angle (°)
0.43	16	180
0.76	1.8	180
0.76	5.3	180
0.76	16	180
0.76	33	180
1.22	16	180

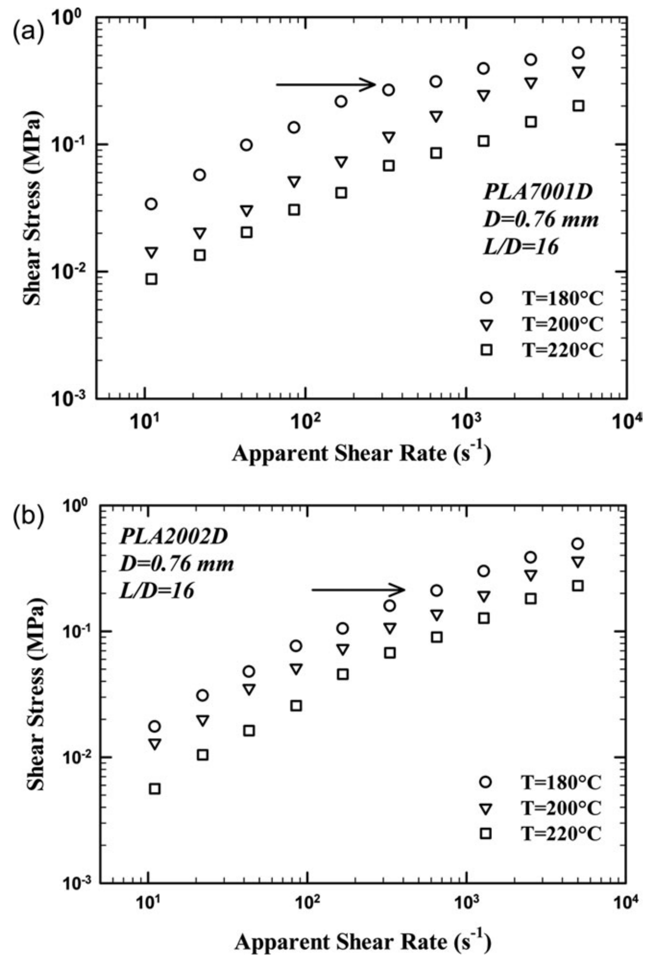

Figure 1. (a) The flow curves of PLA7001D at various temperatures from 180°C to 220°C. The arrow indicates the critical shear stress for the onset of sharkskin. (b) The flow curves of PLA2002D at various temperatures from 180°C to 220°C. The arrow indicates the critical shear stress for the onset of sharkskin.

from the linear viscoelastic measurements. Bagley correction has been applied for this resin by using dies with different L/Ds with the same diameter. The arrow depicts the critical shear stress for the onset of sharkskin as the first type of melt fracture seen here. Figure 2 shows images of extrudates of PLA2002D obtained by extrusion through a capillary die having a diameter of 0.76 mm and L/D of 16 at 180°C, 200°C, and 220°C at various shear rates. First at 180°C, the extrudate has a smooth surface at the shear rate of 650 s^{-1} (Figure 2). As the apparent shear rate increases surface irregularities appear at 1285 s^{-1}, which become gross distortions at 5000 s^{-1}. However, as temperature increases to 200°C and 220°C, no further surface distortions could be seen, even at the highest shear rate of 5000 s^{-1}.

Tables III and IV list the critical shear stresses and rates for the onset of extrudate distortion at the temperature of 180°C for PLA7001D and 2002D, respectively. It is found that the critical shear rate depends significantly on the die diameter. Namely, the critical shear rate for the onset of extrudate distortion decreases with increase of diameter, according to the scaling of

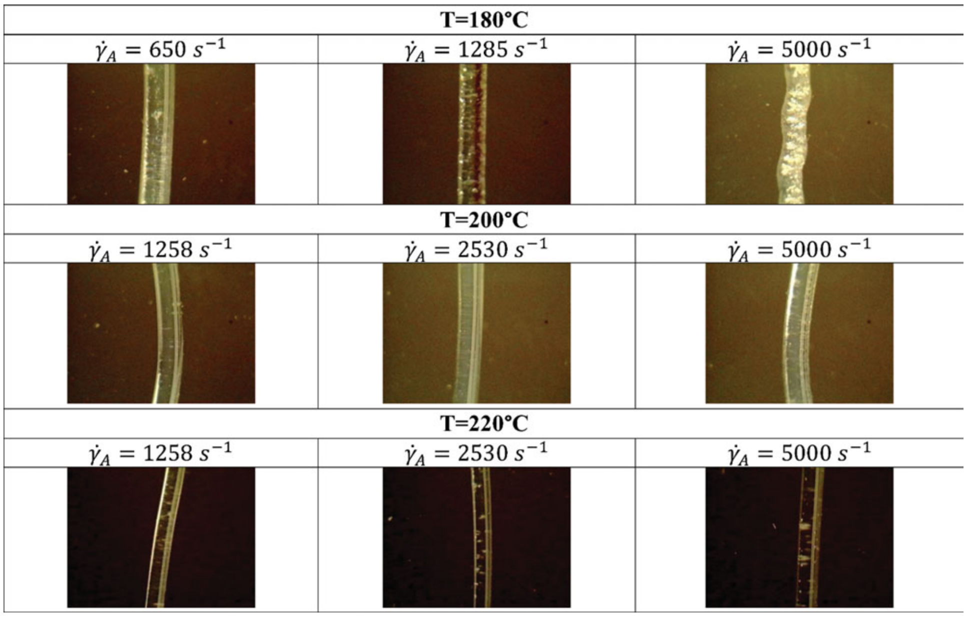

Figure 2. Images of PLA2002D extrudates at different apparent shear rates and various temperatures ranging from 180°C to 220°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\dot{\gamma}_{A,c} \propto D^{-1}$, proposed by Howells and Benbow.[31] However, the critical condition for the onset of melt fracture is not sensitive to L/D ratio, also reported by Migler.[16] No instabilities were observed for PLA3251D at the temperature of 180°C even at very high shear rates reached in this study. This is mainly due to its low molecular weight (about 55,400 g mol^{-1}) and presence of lubricant in the manufactured resin.

The Flow Curve and Melt Fracture of PCL

Capillary extrusion experiments were also performed for the PCL listed in Table I at several temperatures. Figure 3 plots the flow curves of PCL6800 at 120°C, 160°C, 180°C, and 200°C and shear rates in the range of 44 to 1000 s^{-1}. Figure 4 shows typical extrudate images at different shear rates and various temperatures. As the temperature increased from 120°C to 200°C, the critical shear rate is postponed to higher shear rates (from 51 to 502 s^{-1}), although the critical shear stress is about constant (0.20 MPa). Table V summarizes the critical shear rates and stresses at various temperatures for PCL6800 for a capillary die with $D = 0.76$ mm and $L/D = 16$.

Table III. Critical Shear Stress and Critical Apparent Shear Rates for the Onset of Sharkskin of PLA 7001D at 180°C as a Function of the Geometrical Characteristics of Capillary Dies

Die diameter (mm)	L/D	Critical shear stress (MPa)	Critical apparent shear rate, $\dot{\gamma}_{A,c}$ (s^{-1})
0.43	16	0.33	914
0.76	1.8	0.30	463
0.76	5.3	0.29	463
0.76	16	0.29	463
0.76	33	0.30	463
1.22	16	0.20	119

Processing Aids for PLAs and PCLs

As discussed above, the main objective of this work was to identify appropriate processing aids for the extrusion of PLA and PCL. As stressed by Rosenbaum et al.,[32] a potential polymer to work as a processing aid for the extrusion of another polymer should first be immiscible and have an interfacial tension with the polymer under flow smaller than the interfacial tension of the polymer under flow with the wall. Such a candidate might be a PCL for the extrusion of PLA polymer of about similar viscosity and vice versa a PLA for the extrusion of PCL. As it is known PLA is immiscible with PCL and their interfacial tension is small, that is, 1.206 mNm^{-1}.[33–37]

PCL as a Processing Aid for PLA. Extrusion experiments were performed for PLA7001D with addition of 0.5 wt % of PCL6800 (see above for more details). The two polymers were ground and mixed in dry form and then loaded into the barrel of the capillary rheometer. The capillary die was cleaned by placing it for a few minutes into an oven at about 300°C to degrade any polymeric remains off the walls of the die. Figure 5

Table IV. Critical Shear Stress and Critical Apparent Shear Rates for the Onset of Sharkskin of PLA PLA2002D at 180°C as a Function of the Geometrical Characteristics of Capillary Dies

Die diameter (mm)	L/D	Critical shear stress (MPa)	Critical apparent shear rate, $\dot{\gamma}_{A,c}$ (s^{-1})
0.43	16	0.31	1285
0.76	1.8	0.26	914
0.76	5.3	0.26	914
0.76	16	0.25	914
0.76	33	0.26	914
1.22	16	0.23	463

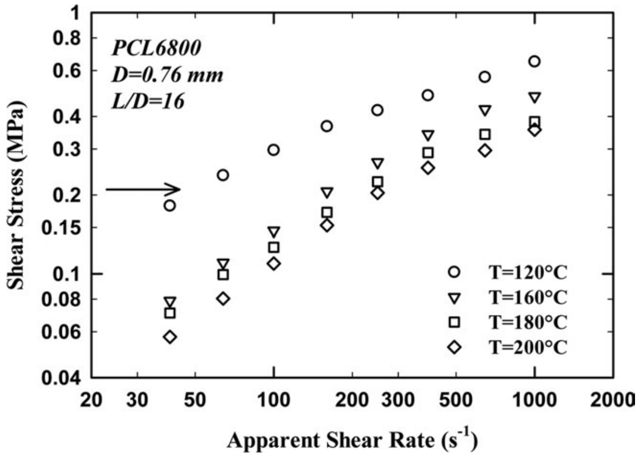

Figure 3. The flow curves of PCL6800 at various temperatures from 120°C to 200°C. The arrow indicates the critical shear stress for the onset of sharkskin.

Table V. Critical Shear Stress and Critical Apparent Shear Rates for the Onset of Sharkskin of PCL6800 at Various Temperatures for a Capillary Die with D = 0.76 mm and L/D = 16

Temperature (°C)	Critical shear stress (MPa)	Critical apparent shear rate, $\dot{\gamma}_{A,c}$ (s^{-1})
120	0.21	51
130	0.20	80
145	0.19	100
160	0.21	160
180	0.20	200
200	0.26	502

depicts a transient experiment illustrating the process of wall coating by the presence of PCL. First, Figure 5 (dashed line) shows the pressure transient for the capillary extrusion of pure PLA7001 by using a die having a diameter equal to 0.76 mm and L/D ratio of 16. The pressure drop increases slowly and after a certain time assumes a steady-state value. When the blend of PLA+0.5% PCL is extruded through a die (Figure 5, continuous lines), the pressure drop passes through a maximum and as the PCL coats gradually the interface, slip becomes a factor and as a result the pressure drop starts decreasing. The steady-state value is obtained after filling the reservoir several times (four times). The steady-state value of the apparent shear stress in the presence of 0.5 wt % of PCL6800 is significantly lower compared with that in the absence of PCL. This is due to the occurrence of slip. The time required to obtain steady-state is defined as the induction time and this is typically the time needed to eliminate melt fracture (time to obtain the full effect of the processing aid).

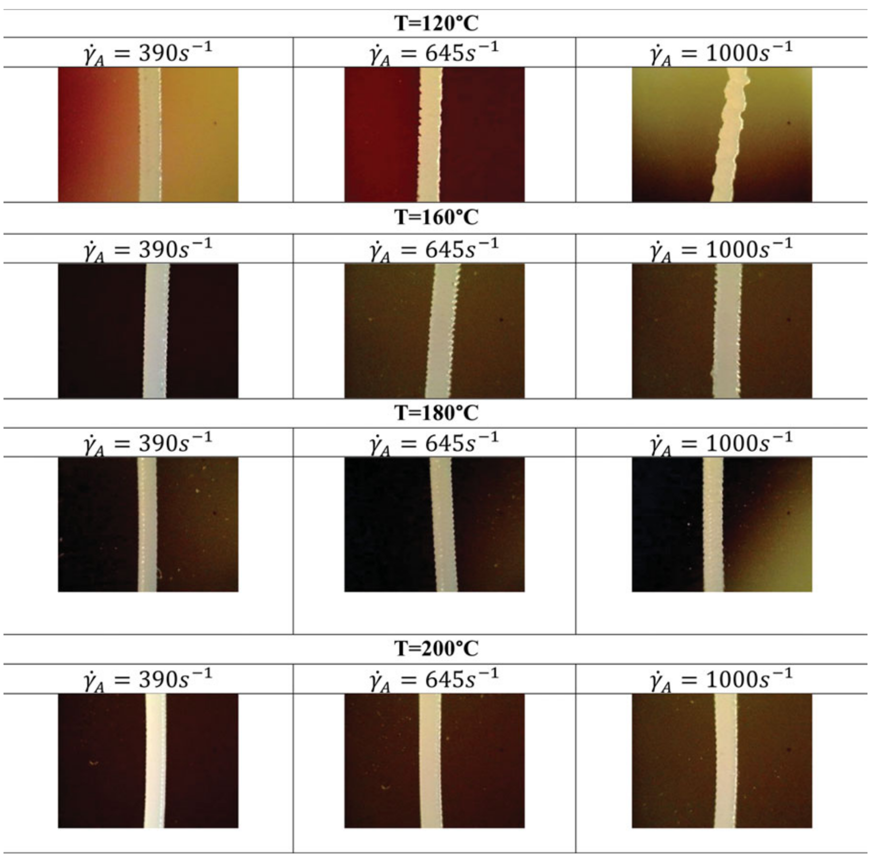

Figure 4. Images of PCL6800 extrudates at different apparent shear rates and various temperatures ranging from 120°C to 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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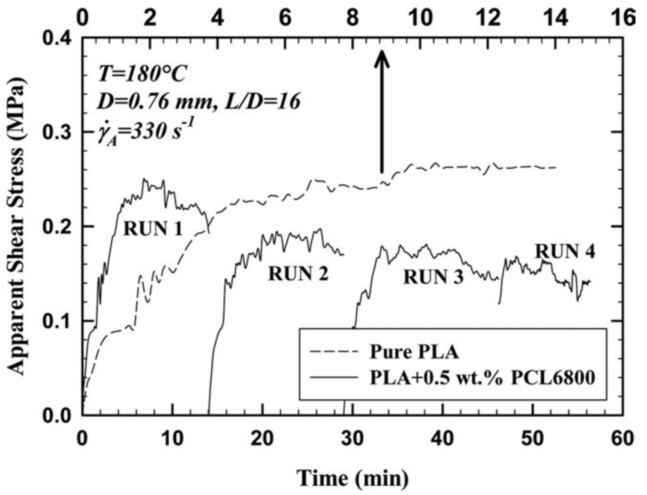

Figure 5. The effect of the addition of 0.5 wt % of a poly(ε-caprolactone) (PCL6800) on the transient response in the capillary extrusion of PLA7001D at 180°C, $\dot{\gamma}_A = 330\ s^{-1}$, $L/D = 16$, and $D = 0.76$ mm.

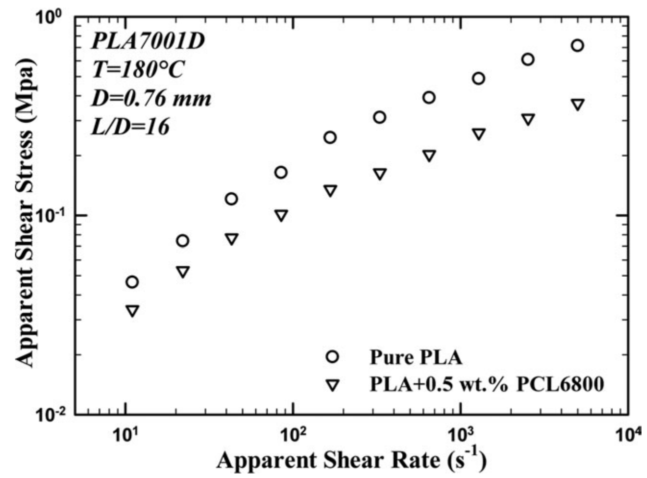

Figure 6. The effect of the addition of 0.5 wt % of a poly(ε-caprolactone) (PCL6800) on the flow curve of resin PLA7001D at 180°C using a die with $D = 0.76$ mm and $L/D = 16$.

Figure 6 shows the apparent flow curves obtained at 180°C for pure PLA7001D and that of a blend of PLA7001D with 0.5 wt % of the finely dispersed PCL6800. The presence of PCL dramatically decreases the shear stress practically over the whole range of apparent shear rates up to 5000 s^{-1}. The presence of PCL eliminates completely melt fracture. Thus, the extrudates appear relatively smooth up to the shear rates of 5000 s^{-1} as can be seen from Figure 7.

PLA as a Processing Aid for PCL. The effect of adding a small amount of PLA7001 to extrude PCL6800 was also studied. The extrusion of pure PCL was followed by adding a small amount of 0.5% PLA7001D. To allow comparison between using PCL as an additive and using PLA as an additive, the extrusion was performed at the temperature of 180°C (above the melting point of PLA) and a die with a diameter 0.76 mm and $L/D = 16$ was used. It is again believed that the PLA coats the wall of the die to act as a processing aid, consequently promotes slip and thus causes a significant drop in the extrusion pressure. Thus, an improved processability can be demonstrated. Experiments at temperatures below the melting point of PLA did not exhibit the effect presented below.

Figure 8 shows the difference between the pressure obtained when extruding pure PCL6800 and extruding PCL with 0.5 wt % PLA7001D. The reduction of the apparent shear stress (or pressure) is significant (from 0.32 MPa to about 0.2 MPa) and the induction time to obtain steady-state is a few minutes (about 15 min). This result shows that indeed PLA can be used

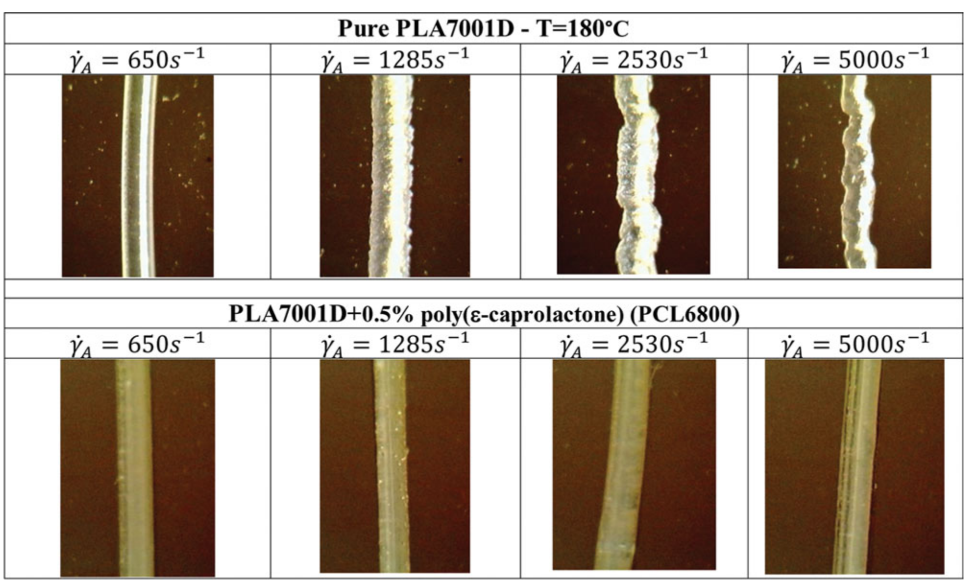

Figure 7. Images of PLA7001D extrudates at different apparent shear rates extruded with and without 0.5 wt % of a poly(ε-caprolactone) (PCL6800) at 180°C. The addition of a PCL is an effective way to eliminate melt fracture in the extrusion of PCL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

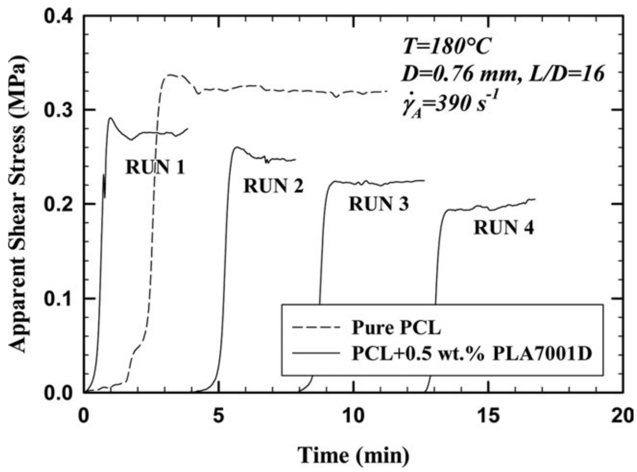

Figure 8. The effect of the addition of 0.5 wt % of a PLA7001D on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 390\,\mathrm{s}^{-1}$, $L/D = 16$, and $D = 0.76$ mm.

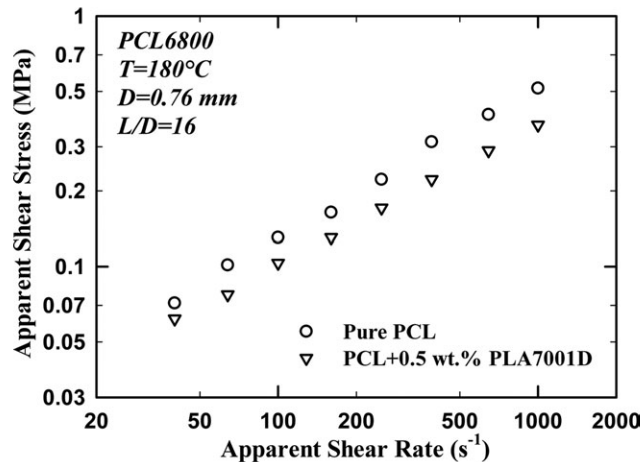

Figure 9. The effect of the addition of 0.5 wt % of PLA7001D on the flow curve of resin PCL6800 at180°C using a die with $D = 0.76$ mm and $L/D = 16$.

as a processing aid for PCL as much as PCL can be used as a processing aid for PLA.

Figure 9 shows the difference between the flow curves of pure PCL and PCL with the addition of 0.5 wt % of PLA7001D. At all tested shear rates, there is a significant reduction in the extrusion pressure of apparent shear rate. Finally, Figure 10 demonstrates the difference in the extrudate appearance of pure PCL and the PCL with 0.5 wt % of PLA7001D. Even at higher shear rates, the extrudates of PCL are relatively smooth with the help of PLA.

Dependence of Induction Time to Obtain Steady-State

In this section, the time required (induction time) to obtain steady-state response for various cases is examined. Three important parameters were investigated, namely the molecular weight of the polymer used as processing aid, the apparent shear rate and the length-to-diameter ratio of the die (L/D). All the experiments were performed for PCL6800, and it is assumed that the results also apply for the extrusion of PLA.

Effect of Molecular Weight of Processing Aid. Two different PLA polymers having different molecular weight were used as additives to extrude PCL6800. All other parameters were kept the same; the extrusion temperature was set at 180°C and the die diameter was 0.76 mm with an L/D ratio of 16. First, the PCL was blended with 0.5 wt % of PLA7001D and PLA3251 (molecular weight of 110.1 × 10^3 g mol^{-1} and 55.4 × 10^3 g mol^{-1}, respectively), and it was extruded until a steady-state was reached. Immediately, after each experiment using a different material the die (heated at 300°C for a few minutes) and the barrel of the capillary rheometer were cleaned thoroughly.

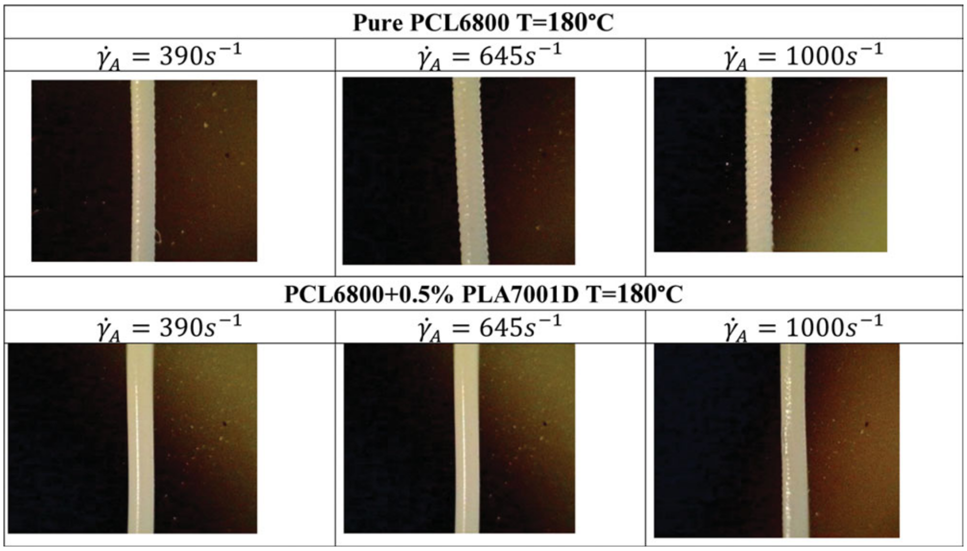

Figure 10. Images of PCL6800 extrudates at different apparent shear rates extruded with and without 0.5 wt % of a PLA7001D at 180°C. The addition of PLA7001D is an effective way to eliminate melt fracture in the extrusion of PCL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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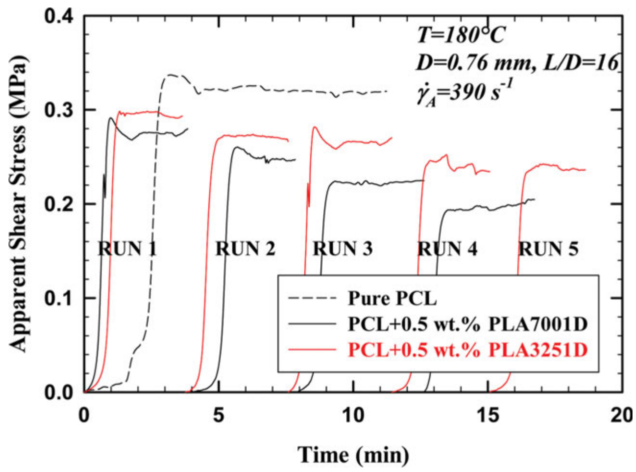

Figure 11. The effect of the addition of 0.5 wt % of a PLA7001D and PLA3251 on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 390\,s^{-1}$, $L/D = 16$, and $D = 0.76$ mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The time required to obtain the steady-state response was found to be a few minutes shorter by using the higher molecular weight PLA as shown in Figure 11.

However, it is worth mentioning that using PLA7001D the reduction in the pressure drop was higher than that in the case of using PLA3251. This also can be shown when comparing the flow curves plotted in Figure 12.

Effect of Apparent Shear Rate. The effect of the apparent shear rate on the time required to reach steady-state was also investigated. The extrusion was performed at the temperature 180°C with a capillary die having a diameter of 0.76 mm and L/D ratio of 16. PCL was blended with 0.5 wt % PLA7001, and the extrusion was performed at two different apparent shear rates of 160 and 1000 s^{-1}. The results are plotted in Figure 13(a, b). It was found that the induction time decreases with increase of

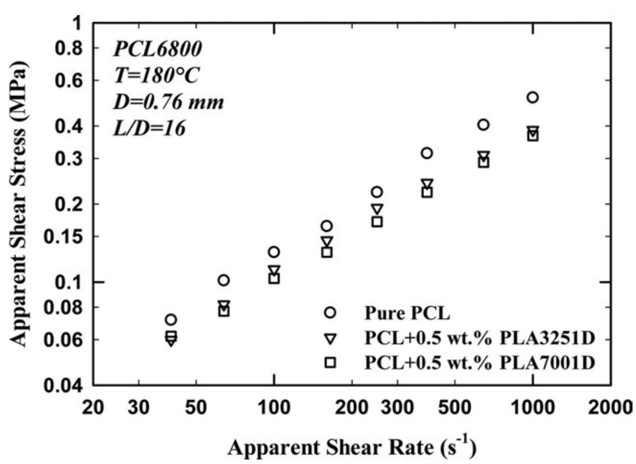

Figure 12. The effect of the addition of 0.5 wt % of PLA7001D and PLA3251 on the flow curve of resin PCL6800 at 180°C using a die with $D = 0.76$ mm and $L/D = 16$.

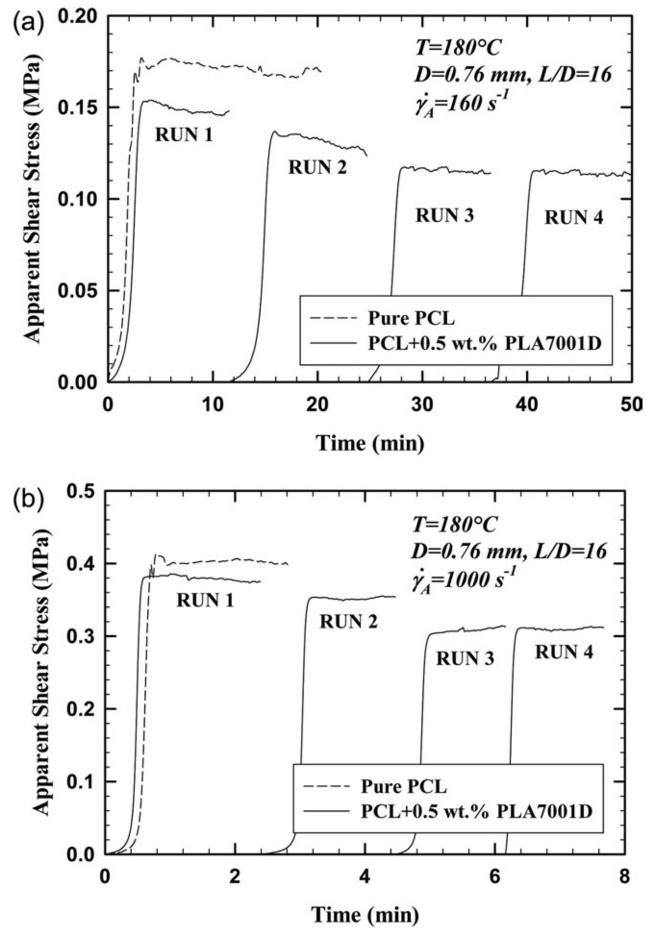

Figure 13. (a) The effect of the addition of 0.5 wt % of a PLA7001D on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 160\,s^{-1}$, $L/D = 16$, and $D = 0.76$ mm. (b) The effect of the addition of 0.5 wt % of a PLA7001D on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 1000\,s^{-1}$, $L/D = 16$, and $D = 0.76$ mm.

the apparent shear rate. It is about 30 and 5 min for shear rates 160 and 1000 s^{-1}, respectively.

Effect of the Length-to Diameter Ratio. To investigate the effect of the length-to-diameter ratio of the die on the time required to reach steady-state, two dies with the same diameter but different L/D ratio were used. The extrusion was performed using a PCL/PLA blend where 0.5 wt % of PLA7001D was added to the PCL. Furthermore, the extrusion temperature was set at 180°C and the apparent shear rate at 390 s^{-1}. It was found that when the L/D was decreased, less time was required to fully coat the die to reach steady-state. This is due to the fact that when increasing the length of the die the overall surface area of the die is increased; thus more time is needed for complete coating as the coating process starts at the entry and the melted additive is slowly convected along the wall. This can be shown by comparing the results in Figure 14(a, b) below.

Fluoropolymer as a Processing Aid

Fluoropolymers are traditional processing aids used in the extrusion of polyethylenes to enhance their processabilities; they

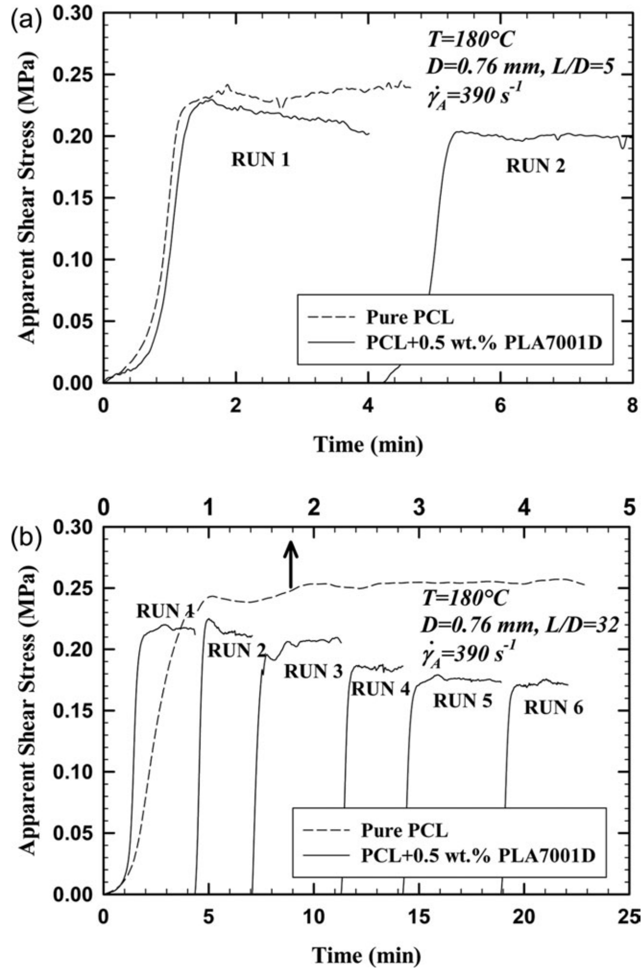

Figure 14. (a) The effect of the addition of 0.5 wt % of a PLA7001D on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 390\,\text{s}^{-1}$, $L/D = 5$, and $D = 0.76$ mm. (b) The effect of the addition of 0.5 wt % of a PLA7001D on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 390\,\text{s}^{-1}$, $L/D = 32$, and $D = 0.76$ mm. Note that as it is indicated by arrow, the top axis belongs to pure PCL data.

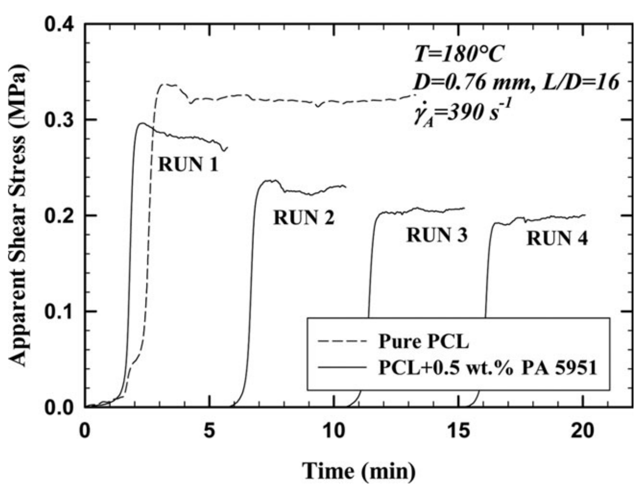

Figure 15. The effect of the addition of 0.5 wt % of a PA 5951 on the transient response in the capillary extrusion of PCL6800 at 180°C, $\dot{\gamma}_A = 390\,\text{s}^{-1}$, $L/D = 16$, and $D = 0.76$ mm.

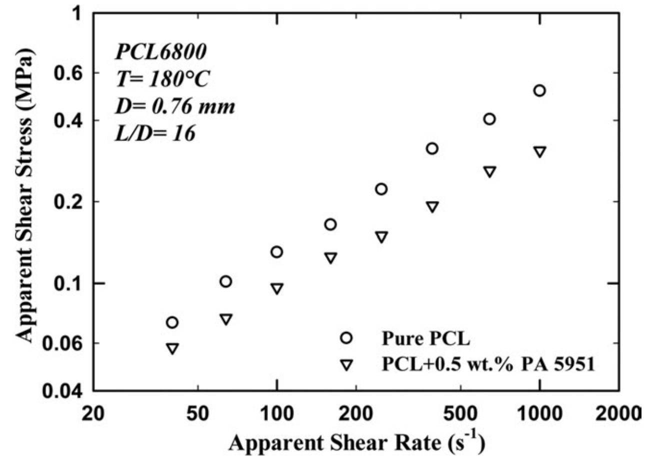

Figure 16. The effect of the addition of 0.5 wt % of PA 5951 on the flow curve of resin PCL6800 at 180°C using a die with $D = 0.76$ mm and $L/D = 16$.

are known to promote slip at the die wall. To see how effective they are in the case of PCL as a processing aid, 0.5 wt % of a fluoropolymer (PA 5951) was used in the capillary extrusion of PCL6800 prepared and extruded at 180°C. It was found that fluoropolymers induced a significant reduction in the extrusion pressure of PCL, thus promoting slip as in the case of polyethylenes.[22,38] The pressure drop was decreased by 36% compared with about 32% caused by the use of PLA7001D as processing aid. This can be shown in Figure 15. Figure 16 shows that the fluoropolymer reduces the extrusion pressure at all shear rates tested, comparing the flow curves of pure PCL6800 and that with the addition of 0.5 wt % PA 5951.

CONCLUSIONS

The melt fracture behavior of a few commercial PLAs and PCL has been investigated by using capillary rheometry. The onset of melt fracture for the high molecular weight PLAs was found to occur at around 0.2–0.3 MPa and around 0.2 MPa for PCL, depending on the geometrical characteristics of the dies and nearly independent of temperature. The critical shear rate for the onset of melt fracture was found to scale inversely proportional with the die diameter consistent with observations on the melt fracture of other polymers such as polyethylenes.

Furthermore, the effect of adding a small amount of 0.5 wt % of PCL into PLA and vice versa on their processability has been studied. It was found that a considerable pressure drop is caused, accompanied by elimination of processing defects and postponement to higher shear rates. Finally, it was shown that a fluoropolymer traditionally used as a processing aid for polyethylenes, worked effectively in the capillary extrusion of PLA as a processing aid.

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